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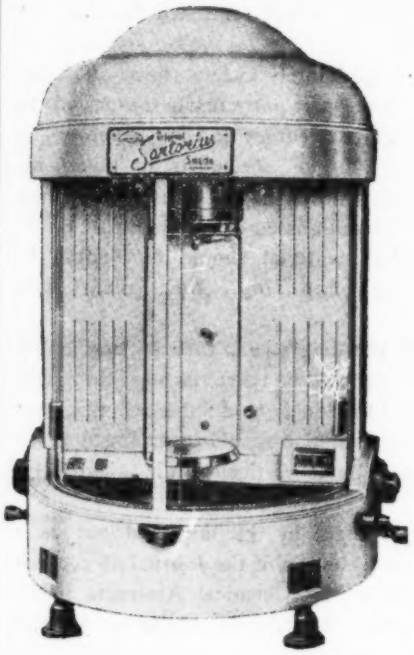

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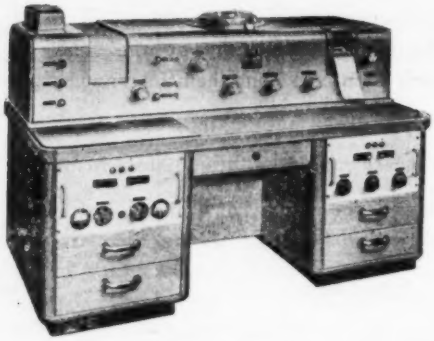

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[Jour. Indian Chem. Soc., Vol. 36, No. 2, 1959]

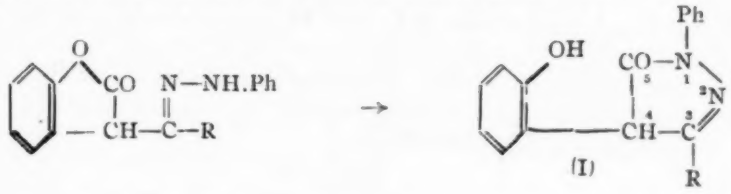
SYNTHESES OF FURANO COMPOUNDS. PART XV. 3-ACYL*iso*-COUMARANONES AND THE REARRANGEMENT OF THEIR PHENYLHYDRAZONES

By J. N. Chatterjea

It has been shown that the phenylhydrazones of 3-acyl*iso*coumaranones undergo facile rearrangement to the related pyrazolones. The acyl derivatives have been prepared by the action of *NN'*-diarylamidines on *iso*coumaranone.

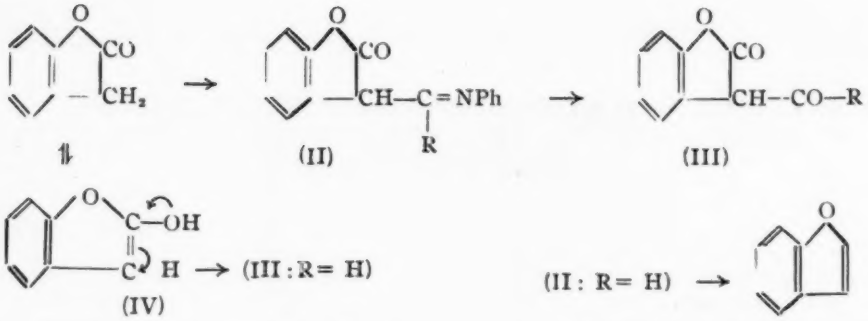
3:4-7:8-Dibenzonaphthyrone has been obtained by the action of pyridine on *iso*coumaranone. *s-tris*-Coumaronobenzene and tribenzoylenebenzene have been similarly obtained. The preparation of some polymethine compounds derived from pyridine has been studied.

In a projected synthesis of some furano-indoles by the obvious application of Fischer's indole synthesis, the phenylhydrazones of 3-acyl*iso*coumaranones were required. The phenylhydrazones could easily be prepared by treating the solution of ketones in cold alcohol with phenylhydrazine, but they were labile in nature; in each case, these underwent rearrangement to pyrazolones, as shown below, either by hydrogen chloride or in some cases by the application of heat. In the case of 3-benzoyl*iso*coumaranone, its normal product with phenylhydrazine is the pyrazolone (I: R= Ph).



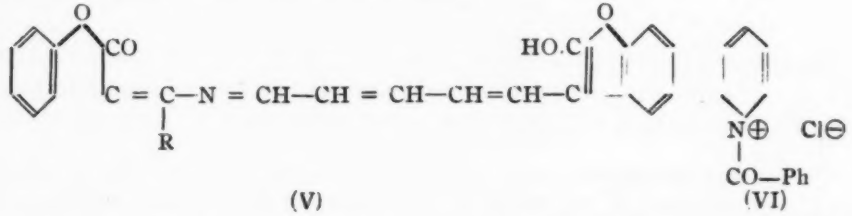
The above result brings it in line with similar results obtained by Glauert and Mann (*J. Chem. Soc.*, 1952, 2401) in the related compounds derived from thio-oxindoles and that of Alberti (*Gazzetta*, 1947, **77**, 398) in the case of the phenylhydrazones of 3-acylindoles.

The acyl*iso*coumaranones were prepared by the previously published method (this *Journal*, 1956, **33**, 175) by the action of acid anhydride and the corresponding sodium salt on *iso*coumaranone. Alternatively, these were also prepared by the action of *NN'*-diarylamidines on *iso*coumaranone whereby the anils of the corresponding acyl derivatives were directly prepared (cf. Glauert and Mann, *J. Chem Soc.*, 1952, 2127). For example, *NN'*-diphenylformamidine (Piggott and Rodd, B.P. 344, 409/1929) and *iso*coumaranone gave the anil (II: R= H) which on hydrolysis by alkali afforded 3-formyl*iso*coumaranone (III: R= H). This aldehyde was also obtained in a low yield by the direct Gattermann synthesis with *iso*coumaranone. The entry of the formyl group in 3-position is explained by assuming *iso*coumaranone to react in the enolic form (IV) whereby the activation at the 3-position is readily understood. 3-Acetyl- and 3-benzoyl-*iso*coumaranones were prepared by the action of *NN'*-diphenylacetamidine and *NN'*-diphenylbenzamidine respectively.



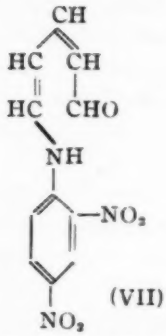
The acid-catalysed rearrangement of acyl*iso*coumaranones (Chatterjea, this *Journal*, 1957, **34**, 299) could as well be applied on the anils. *iso*Coumaranone-3-aldehyde anil, for example, on boiling with hydrochloric acid underwent hydrolysis, decarboxylation and rearrangement to benzofuran.

It remains to mention that acylation of *iso*coumaranone with acid chlorides in pyridine furnishes a different result. Pfeiffer and Enders (*Chem. Ber.*, 1951, **84**, 313) had obtained a product, $C_{28}H_{19}O_4N$, formulated as (V : R = Ph) by the action of benzoyl chloride on *iso*coumaranone in pyridine ; this compound was also isolated in this laboratory by the action of excess of benzoyl chloride on *o*-hydroxyphenylacetic acid in warm pyridine. The formation of (V) obviously involves the opening of the pyridine ring of the complex benzoylpyridinium chloride (VI) (Prey, *Ber.*, 1942, **75**, 537 ; cf. Dennstedt and Zimmermann, *Ber.*, 1886, **19**, 75), but the exclusive formation of the compounds of the type (V) with *iso*coumaranone alone is intriguing for the obvious reason that *iso*coumaranone could neither be replaced by coumaranone, thio-oxindole, etc. nor could the complex of the type (VI) be replaced by *p*-nitrobenzylpyridinium chloride or a ψ-base salt such as cotarnine hydrochloride.

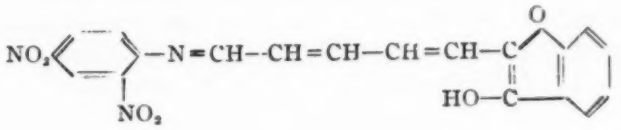


A few polymethine compounds of the type (V) have been prepared with different acid chlorides ; in most of the preparations, the formation of a yellow byproduct, $C_{16}H_8O_4$, m.p. 305°, identified as 3 : 4-7 : 8-dibenzonaphthyrone (*vide infra*) was noted. Compounds analogous to (V) are available by the condensation of Zincke's aldehyde (VII) (Zincke *et al.*, *Annalen*, 1904, **330**, 367 ; 1904, **333**, 296 ; 1905, **338**, 107 ; Fischer and Hamer, *J. Chem. Soc.*, 1933, 189 ; Pfeiffer and Enders, *loc. cit.*) with reactive methylene groups. For example, the aldehyde gave the polymethine compound (VIII) with coumaranone in warm pyridine ; similar products were also obtained by employing thioindoxyl, 1 : 3-diketohydrindene, etc. Both the classes of compounds (V) and (VIII) are characterised by a colour reaction involving the dilution

of the polymethine compound in pyridine with further amount of the solvent. In each case, the colour changes from red or brownish red to blue or green. The change is reversible and doubtlessly involves the mobility of the prototropic system.

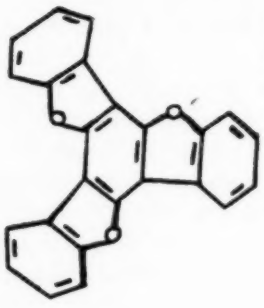


(VII)

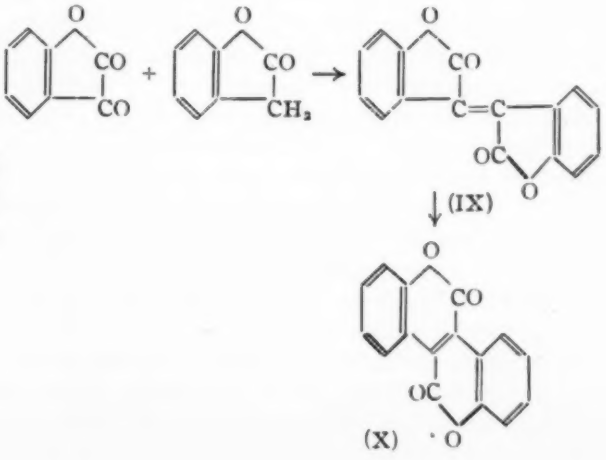


(VIII)

The origin of the yellow byproduct, mentioned above, was traced as due to the action of warm pyridine on *iso*coumaranone itself. The compound shows a lactone carbonyl absorption at 5.80 μ in the infra-red and exhibits an intense absorption at 381 mμ in the ultraviolet. On catalytic hydrogenation one mole of hydrogen was absorbed, affording a mixture of colorless stereoisomerides from which one component was isolated in pure condition. From these results it appears that the compound is 3:4-7:8 dibenzonaphthyrone (X) which has, indeed, been confirmed by condensing *iso*coumaranone with coumarandione according to Chovin (*Compt. rend.*, 1941, **212**, 549 ; 1942, **215**, 466 ; *Bull. soc. chim.*, 1944, **11**, 82) to *iso*oxindigo (IX) which has been found to isomerise to (X) with the aid of warm pyridine. *iso*Oxindigo has a lactone carbonyl absorption at 5.66 μ as expected for the smaller five-membered ring and a moderately intense absorption in the ultraviolet on account of lesser conjugation. *iso*Coumaranone absorbs at 5.55μ and is practically transparent in U V. (cf. Glauert and Mann, *J. Chem. Soc.*, 1955, 2537, for I. R. absorption of thio-oxindole).



(XI)



(X)

Thio-oxindole, the sulphur analogue of *iso*coumaranone, gave only intractable tar with warm pyridine. Coumaranone, on similar treatment, gave a poor yield of a compound, $(C_8H_4O)_n$, which appears to be identical with Fries and Pfaffendorf's (*Ber.*, 1910, **43**, 212; 1911, **44**, 114) compound, $C_{32}H_{16}O_4$, which according to the results of Baker and Banks, (*J. Chem. Soc.*, 1939, 279), should be modified to $C_{24}H_{12}O_3$ and formulated as (XI). 1:3-Diketohydrindene on treatment with pyridine afforded tribenzoylenebenzene (XI: CO in place of O) isolated before by Kostanecki and Laczkowski (*Ber.*, 1897, **30**, 2138) by other methods.

EXPERIMENTAL

*iso*Coumaranone was prepared by the cyclisation of *o*-hydroxyphenylacetic acid. The compound is practically transparent in U. V. $\lambda_{alc.}^{max}$ 271 mμ (ε 1,196); 277 mμ (ε 1,160). I. R. spectrum: Carbonyl absorption at 5.55 μ (rather low).

3-*Formylcoumaranone*-2. *Method* (*a*).—A mixture of *iso*coumaranone (1.0 g.), diphenylformamidine (1.4 g., prepared according to Shoesmith and Haldane, *J. Chem. Soc.*, 1923, **123**, 2704) was heated in an oil-bath at 150° for 45 mins. Aniline was liberated. The melt was treated with alcohol when the *anil* (II: R=H; 1.4 g.) separated. It was crystallised from alcohol in yellow plates, m.p. 160-61°. (Found: N, 5.5. $C_{18}H_{11}O_2N$ requires N, 5.9%). The anil (2.5 g.) was boiled with NaOH (20 c.c., 10%) for 4 to 5 minutes, filtered hot from the unchanged residue and the filtrate cooled in ice.

The *sodium salt* separating was collected, washed with NaOH solution, dissolved in water and acidified. Colourless crystals of the *aldehyde* (0.85 g.) separated which was crystallised from dilute alcohol in colorless needles, m.p. 169°. (Found: C, 66.7; H, 4.0. $C_9H_6O_3$ requires C, 66.7; H, 3.7 %). With ferric chloride the compound gave a deep blue coloration and gave a grey *copper chelate* with copper sulphate.

The *phenylhydrazone* was obtained by adding phenylhydrazine (0.3 g.) to a cold solution of the aldehyde (0.5 g.) in alcohol (3 c.c.). After a minute, nearly colorless crystals of the phenylhydrazone (0.4 g.) separated, which on quick crystallisation from alcohol was obtained in cream-coloured prisms, m.p. 176° (quick heating), the melt solidifying again and remelting at 233°, corresponding to the m.p. of the pyrazolone (I: R=H). (Found: N, 10.8. $C_{15}H_{12}O_2N_2$ requires N, 11.1%). With ferric chloride the compound gave an orange-red coloration.

Method (*b*).—A mixture of *iso*coumaranone (1.0 g.) in ether (10 c.c.) was treated with hydrogen cyanide (1.0 g.) and saturated at 0° with dry hydrogen chloride. The mixture was left overnight, the colorless crystalline mass collected, boiled with alkali (5 c.c., 10%) for 2 minutes, acidified and extracted with ether. The residue, which partly solidified on purification, gave the above aldehyde, m.p. 169°.

Coumarone.—The foregoing anil (0.4 g) was boiled with a mixture of acetic acid (3 c.c.) and HCl (0.3 c.c.) for 4 hours. The mixture on working up afforded coumarone (0.1 g.), b.p. 170°; picrate, m.p. 102° (lit., 102-103°).

3-*Acetylcoumaranone*-2.—A mixture of *iso*coumaranone (1 g.), diphenylacetamidine (1.5 g., prepared according to Sen and Roy, *J. Chem. Soc.*, 1926, 646) was heated at 150-60° for 2 hours. On adding alcohol to the melt, the *anil* (II: R= Me; 1.1 g.)

* All m. p. s are uncorrected.

separated which was crystallised from alcohol in colorless needles, m.p. 134°. (Found: N, 6.1. $C_{16}H_{13}O_2N$ requires N, 5.6%). The anil (0.5 g.) in alcohol (3 c.c.) was boiled with alkali (5 c.c., 10%) for 3 minutes, the alcohol removed by distillation, the residue diluted with water, filtered and acidified, affording 3-acetyl*iso*coumaranone (0.25 g.), which was crystallised from dilute alcohol in colorless needles, m.p. and mixed m.p. 135-36°. (Found: C, 68.0; H, 4.9. Calc. for $C_{10}H_8O_3$: C, 68.1; H, 4.5%).

The *phenylhydrazone*, prepared in the cold, was crystallised from alcohol in colorless leaflets, m.p. 170°, developing an orange coloration with ferric chloride. (Found: N, 9.9. $C_{16}H_{14}O_2N_2$ requires N, 10.5%).

3-*Benzoylcoumaranone*-2.—A mixture of *NN'*-diphenylbenzamidine (0.75 g., Beilstein, 4th. ed., Vol. XII, p. 273) and *iso*coumaranone (0.5 g.) was heated at 140-50° for 2½ hours. On adding alcohol to the cooled melt the *anil* (II: R= Ph; 0.5 g.) separated. It was crystallised from alcohol in lemon-yellow flat needles, m.p. 209°. (Found: C, 80.0; H, 5.0. $C_{21}H_{15}O_2N$ requires C, 80.5; H, 4.8%). On boiling with alcoholic NaOH solution (10%) for 10 minutes, the product was found to contain much unchanged material along with 2-phenylcoumarone and 3-benzoyl*iso*coumaranone, m.p. 100°. U.V. spectrum of the latter: $\lambda_{alc.}^{max}$ 232 mμ (ε 11,589), 252 mμ (ε 13,169), 339 mμ (ε 11,026). I. R. spectrum (KBr pellet, 1% w/w): λ_{max} 5.93, 6.15, 6.70, 6.91, 7.45, 8.03, 8.24, 8.48, 8.58 and 8.68 μ.

On boiling the anil with AcOH-HCl for 4 hours and adding the colorless solution to water, a bluish precipitate of 2-phenylcoumarone was obtained which crystallised from alcohol in colorless plates, m.p. 121°.

*Action of Phenylhydrazine on 3-Benzoyliso**coumaranone*.—Equivalent amounts of 3-benzoyl*iso*coumaranone and phenylhydrazine in alcohol were left in the refrigerator for 12 days. The impure crystals (m.p. 140-45°) that separated contained mostly the *pyrazolone* (I: R= Ph) because on boiling with EtOH-HCl the same product, m.p. 145° (from alcohol), was obtained. (Found: C, 76.2; H, 5.1. $C_{21}H_{16}O_2N_2$ requires C, 76.8; H, 4.9%). With ferric chloride the compound gave a bluish green colour.

Rearrangement of the Phenylhydrazones to the respective Pyrazolones.—The rearrangement was simply brought about by boiling the phenylhydrazones with EtOH-HCl (10%) for 2 to 3 hours.

3-Formyl*iso*coumaranone phenylhydrazone gave 4-o-*hydroxyphenyl*-1-*phenylpyrazol*-5-*one*, m.p. 233° (from alcohol), showing a light bluish green colour with ferric chloride. (Found: C, 71.1; H, 5.0. $C_{15}H_{12}O_2N_2$ requires C, 71.4; H, 4.8%).

3 Acetyl*iso*coumaranone phenylhydrazone gave 4-o-*hydroxyphenyl*-3-*methyl*-1-*phenylpyrazol*-5-*one* in quantitative yield, m.p. 201-202° (from alcohol), developing a bluish green colour with ferric chloride. (Found: N, 10.2. $C_{16}H_{14}O_2N_2$ requires N, 10.5%).

3-o-*Hydroxyphenylacetyl**isocoumaranone phenylhydrazone*, which was prepared by the action of phenylhydrazine on the self-condensation product of *iso*coumaranone (this *Journal*, 1956, **33**, 175) in the usual way, was crystallised from dilute alcohol in pinkish leaflets, m.p. 201°, solidifying again and remelting at 224°, corresponding to the m.p. of the *pyrazolone* [I: R= $CH_2C_6H_4OH$ (*o*)]. (Found: N, 7.3. $C_{22}H_{18}O_3N_2$ requires N, 7.8%). The phenylhydrazone with EtOH-HCl gave the above pyrazolone crystal-

lising from acetic acid in nearly colorless prisms, m p. 224°, exhibiting a greenish coloration with ferric chloride. (Found : N, 7.2. $C_{22}H_{18}O_3N_2$ requires N, 7.8%).

Action of Substituted Benzoyl Chlorides on iso*Coumaranone in Pyridine.*—A mixture of *p*-toluoyl chloride (2.5 g.) and *iso*coumaranone (2 g.) in pyridine (8 c.c.) was heated on a water-bath for 6 hours. The bluish red solid was collected, washed with ether, hydrochloric acid, water and finally crystallised from pyridine. The *polymethine compound* (V : R= *p*-tolyl) was obtained in bluish red prisms, m.p. 268-69° (decomp.). (Found : C, 78.2 ; H, 5.0. $C_{29}H_{21}O_4N$ requires C, 77.8 ; H, 4 7%). The red colour of the solution of the compound in pyridine became bluish green on dilution with pyridine. With sulphuric acid the compound gave a violet colour.

The *polymethine compound* (V : R= *p*-anisyl), which was similarly prepared, was crystallised from pyridine in bluish red prisms, m.p. 255° (decomp.). (Found : N, 3.4. $C_{29}H_{21}O_5N$ requires N, 3.0%). The reddish colour of the substance in pyridine became deep blue on dilution with pyridine.

The *polymethine compound* (V : R = *m*-chlorophenyl) was similarly prepared and separated from pyridine in steel-blue needles, m.p. 260° (decomp.). (Found : N, 2.6. $C_{28}H_{18}O_4NCl$ requires N, 3.0%). The dilute solution in pyridine was deep blue.

The mother-liquor in these preparations, deposited yellowish needles (or prisms), m.p. 305°, the origin of which was traced as due to self-condensation of *iso*coumaranone as shown below.

Action of Pyridine on (*i*) iso*Cumaranone.*—*iso*Coumaranone (1.5 g.) was dissolved in pyridine (3 c.c.) and heated on a water-bath for 18 hours. Alcohol (2 c.c.) was added to the mixture and it was left in the refrigerator for a week. The yellow needles (*ca.* 30 mg.) were collected and crystallised from acetic acid. The compound was obtained in yellow needles, m.p. 305°, showing a lemon-yellow coloration with H_2SO_4. [Found : C, 73.0, 73 0 ; H, 3.3, 3.4 ; M.W. (Rast), 257. Calc. for $C_{16}H_8O_4$: C, 72.7 ; H, 3.0%. M W. 264]. U.V. spectrum : $\lambda_{alc.}^{max}$ 253 mμ (ε 9,507), 269 mμ (ε 6, 477), 371 mμ (ε 15,060), 381 mμ (ε 15,604) and 401 mμ (shoulder) (ε 9,979). Infra-red spectrum : strong absorption at 5.80μ. The compound was identified with 3 : 4-7 : 8-dibenzonaphthyrone, prepared from *iso*oxindigo as follows : A mixture of coumaran-dione (1.5 g.), *iso*coumaranone (1.4 g.) and phosphorus tribromide (1.8 c.c.) was heated on a water-bath for ½ hour. An orange product separated. The mixture was decomposed carefully with water, the orange crystals collected, washed with alcohol and crystallised from acetic acid. *iso*Oxindigo was obtained in golden yellow plates (1.4 g.), m.p. 283°, developing an orange coloration with H_2SO_4. U.V. spectrum : $\lambda_{alc.}^{max}$ 252 mμ (ε 7,082), 254 mμ (ε 7,075), 395 mμ (ε 7,524) and 433 mμ (ε 7,656). I. R. spectrum : strong absorption at 5.66 μ. When heated with pyridine on the water-bath for 15 hours, the compound was transformed completely into (X), m.p. 305°, identical with the compound derived from *iso*coumaranone.

On hydrogenation with Adams' catalyst in acetic acid, the compound absorbed one mole of hydrogen The resulting colorless gum was probably a mixture of stereoisomerides, from which one component was obtained as colorless plates from acetic acid, m.p. 218°. (Found : C, 72.0 ; H, 3.9. $C_{16}H_{10}O_4$ requires C, 72.2 ; H, 3.8%).

(ii) On Coumaranone.—A solution of coumaranone (1.0 g.) in pyridine (5 c.c.) was heated on the water-bath for 48 hours. The reddish solution was left overnight in the refrigerator. The crystalline mass of *s-tris*-coumaronobenzene (*ca.* 10 mg.) was collected, washed with acetic acid and crystallised from xylene in yellow plates, m.p. > 360°. (Found : C, 82.0 ; H, 3.6. Calc for $C_{24}H_{12}O_3$: C, 82.6 ; H, 3.4%). The compound can be sublimed.

(iii) On 1 : 3-*Diketohydrindene.*—On dissolving the compound (0.5 g.) in pyridine (2 c.c.), a magenta-red solution was obtained. The colour faded on heating on the water-bath for ½ hour and on cooling yellow needles of tribenzoylenebenzene (*ca.* 20 mg.) were obtained, m.p. > 360°, developing orange-red coloration with H_2SO_4. (Found : C, 84.1 ; H, 3.4. Calc. for $C_{27}H_{12}O_3$: C, 84.3; H, 3.1%).

Condensation Reactions of Zincke's Aldehyde

With Coumaranone.—A mixture of coumaranone (0.3 g.), Zincke's aldehyde (0.6 g.) and pyridine (3 c.c.) was heated on the water-bath for 6 hours. The coal-black crystalline mass (0.15 g.) separating was filtered. On crystallisation from pyridine, the *compound* (VIII) was obtained as dark, silky needles, m.p. 232°. (Found : N, 10.7. $C_{19}H_{13}O_6N_3$ requires N, 11.1%). The dilute solution of the compound in pyridine was green.

With Thioindoxyl.—A mixture of Zincke's aldehyde (1.2 g.), thioindoxyl (0.8 g.) and dry pyridine (15 c.c.) was heated on the water-bath for 1 hour and then left overnight. Acetone (6 c.c.) was added to the pasty mass and the black needles of (VIII : S in place of O) filtered. The *compound* (1.5 g.) was obtained in black needles, m.p. 266° (decomp.) from pyridine. (Found : N, 10.0. $C_{19}H_{13}O_5N_3S$ requires N, 10.6%). The violet solution in pyridine became deep blue on dilution with pyridine.

With 1 : 3-*Diketohydrindene.*—The condensation was done as above, but for a shorter period (½ hour). The *compound* (VIII : CO in place of O) was washed with acetone and warm pyridine and obtained in dark needles, m.p. 275° (decomp.). (Found : N, 11.0. $C_{20}H_{13}O_6N_3$ requires N, 10.8%). The solution of the compound in pyridine became blue on dilution with pyridine.

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CHEMICAL LABORATORY,
SCIENCE COLLEGE,
PATNA-5.

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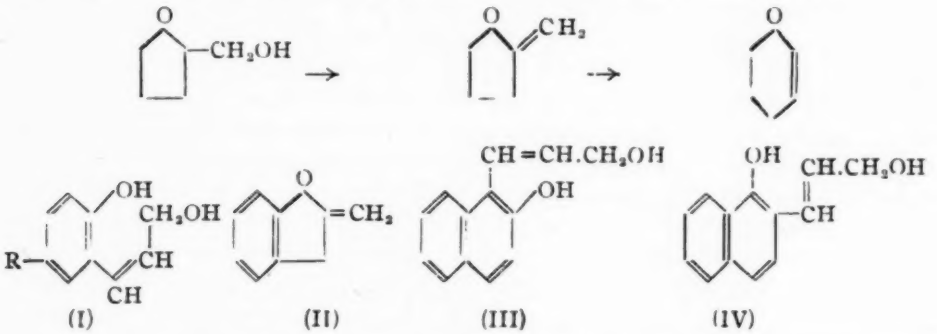
SYNTHESES OF FURANO COMPOUNDS. PART XVI. THERMAL CYCLISATION OF *cis-o*-HYDROXYCINNAMYL ALCOHOLS

By J. N. Chatterjea

A simple method of preparation of 1:2-chromene and its derivatives has been developed by the pyrolysis of *cis-o*-hydroxycinnamyl alcohols. The expected 2-methylenecoumarans are not formed. It is shown that the formylation of chroman furnishes 6-formyl derivative. 2-Methyl-4:5-benzocoumarone and 2-methyl-6:7-benzocoumarone have been synthesised.

Interest in the hitherto-unknown 2-methylenecoumaran (II) prompted the present investigation. Paul (*Bull. soc. chim*, 1933, *iv*, **53**, 1479 1934, *v*, **1**, 971; 1935, **2**, 311, 2220) found that the dehydration of tetrahydrofurfuryl alcohol over alumina at 330-350° yielded dihydropyran by an exothermic reaction, the reaction probably taking place *via* the unsaturated methylene derivative as shown below:

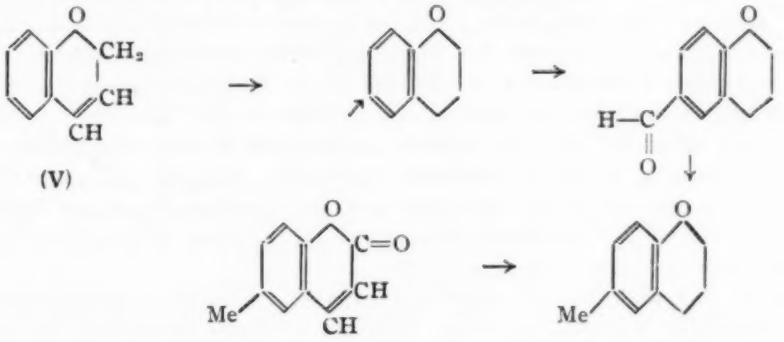


(I) (II) (III) (IV)

It therefore transpired that the 'cyclodehydration' of *cis-o*-hydroxycinnamyl alcohol (I: R= H) might lead to (II).

The alcohol (I: R =H) is now easily accessible by lithium aluminium hydride reduction of coumarin (Karrer and Banerjea, *Helv. Chim. Acta*, 1949, **32**, 1692), and it is now found that lithium borohydride may also be used. 5-Methyl-2-(γ-hydroxypropenyl)-phenol (I: R=Me), 1-(γ-hydroxypropenyl)-2-naphthol (III) and 2-(γ-hydroxypropenyl)-1-naphthol (IV) were prepared from the corresponding coumarins by Karrer and Banerjea's method (*loc. cit.*). The alcohol (I: R=H) was prone to undergo polymerisation with acidic reagents, such as, phosphorus tribromide, thionyl chloride and even with hot aqueous hydrochloric acid. With sodium acetate-acetic anhydride the diacetate was obtained. On dry distillation, however, an alkali-insoluble oil was obtained having the expected composition, C_9H_8O, and similar compounds were also obtained from (I: R=Me), (III) and (IV). These are liquids and characterised by nicely crystalline picrates. *A priori* the compound derived from (I: R=H) may be 2-methylenecoumaran or 2-methylcoumarone or 1:2-chromene (V). However, the product was neither identical with the known 2-methylcoumarone nor

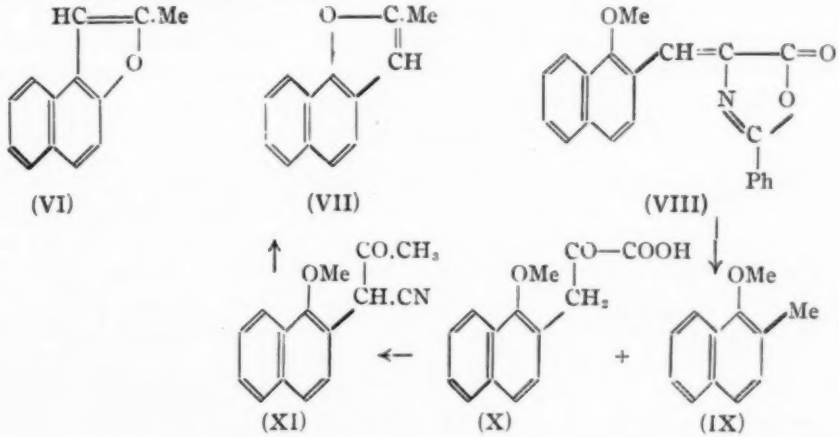
was the methylene structure (II) possible for it, as it did not give any formaldehyde on ozonisation. The compound has been identified with the recently isolated 1 : 2-chromene (Maitte, *Ann. Chim.*, 1954, **9**, 431), and this has been confirmed by catalytic reduction



(V)

to chroman with which it has been identified by direct comparison and by the preparation of a solid derivative of chroman, which involves formylation with dimethylformamide and the preparation of its 2 : 4-dinitrophenylhydrazone. The orientation of the formyl group has been established by the Wolff-Kischner reduction to the known 6-methylchroman (Auwers, *Annalen*, 1918, **415**, 153; Benneville and Connor, *J. Amer. Chem. Soc.*, 1940, **62**, 283, 3067). Chromene also gave a formyl derivative, presumably the 6-formyl compound and 2-methylcoumaran gave the 5-formyl derivative.

The products of thermal cyclisation of (III) and (IV) are, by analogy, 5 : 6-benzo-(1 : 2)-chromene and 7 : 8-benzo-(1 : 2)-chromene respectively and their possibility of being 4 : 5-benzo-2-methylcoumarone (VI) and 6 : 7-benzo-2-methylcoumarone (VII) excluded by their direct synthesis.



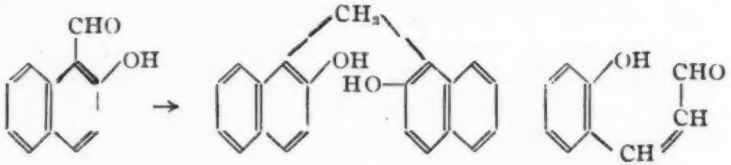
(VI) (VII) (VIII)

(XI) (X) (IX)

The synthesis of (VII) was achieved by starting from the labouriously accessible 1-hydroxy-2-naphthaldehyde (Bezdzik and Friedländer, *Monatsh.*, 1908, **89**, 383; 1909, **30**, 278) which was methylated (optimum yield, 25-35%) and then converted

into the azlactone (VIII). Hydrolysis of this with baryta afforded the α-ketonic acid (X) and 1-methoxy-2-methylnaphthalene (IX) arising by the cleavage of the keto-acid (cf. Burton and Stoves, *J. Chem. Soc.*, 1937, 402). Oximation of the former, followed by treatment with acetic anhydride (Niederl and Ziering, *J. Amer. Chem. Soc.*, 1942, **64**, 885), yielded 1-methoxy-2-naphthylacetonitrile. On the Claisen condensation with ethyl acetate the keto-nitrile (XI) was obtained which afforded (VII) by ketonic hydrolysis. The synthesis of (VI) followed exactly similar lines. In this connection it may be pointed ont that Adams and Rindfusz (*J. Amer. Chem. Soc.*, 1919, **41**, 648) had embarked on the synthesis of 2-methylenecoumarans from *o*-allylphenols, which, as shown by Claisen (*Ber.*, 1920, **53**, 322), really afforded 2-methylcoumarones. This we have confirmed. On this basis Adams and Rindfusz's α-methylene-β-naphthodihydrofuran, m.p. 58°, should be really (VI), but their product is clearly different from ours (m.p. 138-40°).

During this work we had occasion to subject 2-hydroxy-1-naphthaldehyde or the corresponding triacetate to lithium aluminium hydride reduction. The product obtained in each case was *bis*-2-hydroxy-1-naphthylmethane by loss of one carbon atom.



(XII)

Betti and Mendici (*Atti R. Acad. Lincei*, 1904, *v*, **13**, 542 ; *Gazzetta*, 1906, **36**, 655) have pointed out that the reactions of 2-hydroxy-1-naphthaldehyde are characterised by the ease with which the aldehyde group is eliminated, and they have also encountered similar reduction products.

Oxidation of (I: R=H) with manganese dioxide in chloroform gave the aldehyde (XII), but surprisingly it has not been possible to convert this into benzopyrylium salt.

* Experimental

Reduction of Coumarin with Lithium Borohydride.—A solution of coumarin (1.0 g.) in dry ether (60 c.c.) was added to a cooled slurry of lithium borohydride (0.6 g.) in ether (50 c.c.) with mechanical stirring. After allowing to stay in the cold for 15 minutes, the mixture was carefully treated with water, acidified with H_2SO_4 (dil.), the ether layer separated, dried ($MgSO_4$) and the solvent removed. The residue on crystallisation from benzene furnished *cis-o*-hydroxycinnamyl alcohol (0.4 g.) as colorless needles, m.p. 110° (Karrer and Banerjea, *loc. cit.*, report m.p 110°). On treatment with acetic anhydride (6 c.c.) and sodium acetate (0.3 g.), the compound (2.8 g.) gave the *diacetate* (2.8 g.), b.p. 145°/4 mm ; n_D^{33} 1.5143. (Found : C, 66.1 ; H, 5.9. $C_{13}H_{14}O_4$ requires C, 66.7 ; H, 5.9%).

5-Methyl-2-(γ-hydroxypropenyl)-phenol.—A solution of 6-methylcoumarin (1.7 g.) in ether (100 c.c.) was added to a cooled slurry of $LiAlH_4$ (0.9 g.) in

ether (100 c.c.). After 12 minutes the mixture was worked up as above to afford the *phenol* (0.8 g.) which was crystallised as colorless silky needles from benzene, m.p. 123°. (Found: C, 73.2; H, 7.0. $C_{10}H_{12}O_2$ requires C, 73.2; H, 7.3%).

2-(γ-*Hydroxypropenyl*)-1-*naphthol* was similarly prepared from 7:8-benzocoumarin; the reduction, however, was carried out with powdered suspension. The compound (yield 50%) was crystallised from benzene in colorless needles, m.p. 122°. (Found: C, 77.7; H, 5.9. $C_{13}H_{12}O_2$ requires C, 78.0; H, 6.0%).

1-(γ-*Hydroxypropenyl*)-2-*naphthol* was obtained similarly from 5:6-benzocoumarin and was crystallised from benzene in colorless needles, m. p. 129-30°. (Found: C, 77.6; H, 5.5. $C_{13}H_{12}O_2$ requires C, 78.0; H, 6.0%).

1:2-*Chromene*.—*cis-o*-Hydroxycinnamyl alcohol (5.0 g.) was pyrolysed under slight vacuum when water and a colorless distillate passed over leaving a large residue (60%). The distillate contained a small quantity of the unchanged material. The whole was taken up in ether, washed with alkali, dried ($MgSO_4$) and distilled. 1:2-Chromene or 1(2H)-benzopyran was obtained as a colorless mobile liquid (1.0 to 1.3 g.), b.p 132°/102 mm; n_D^{24} 1.5869 (Maitte reports n_D^{16} as 1.5923). The compound gave with H_2SO_4 an orange coloration, turning pink. (Found: C, 82.0; H, 6.2. Calc. for C_9H_8O: C, 81.8; H, 6.8%). U. V. spectrum: λ_{hexane}^{max} 2665 Å and 3140 Å.

The *picrate* was obtained in orange-red prisms, m.p. 70-71° depressed to 60° on admixture with picrate of 2-methylcoumarone (m.p. 74°). (Found: N, 11.0. C_9H_8O. $C_6H_3O_7N_3$ requires N, 11.6%).

Ozonolysis.—A stream of ozonised oxygen (2.5%, 50 c.c./min.) was bubbled through a solution of the substance (0.24 g.) in dry CCl_4 (20 c.c.) till a large excess of ozone could be detected in the exit gas (45 mins.). The ozonide separated out in the form of a colorless waxy solid. After the removal of CCl_4 at the room temperature under reduced pressure, the ozonide was warmed (50°) with water (30 c.c.), zinc dust (0.5 g.) and a trace of acetic acid for 15 minutes. The mixture was filtered and the residue washed with water. The filtrate and the washings gave brownish red 2:4-dinitrophenylhydrazone, which on fractional crystallisation from benzene gave a component, m.p. 238-40° and another, m.p. 110-15° (both from alcohol), but the 2:4-dinitrophenylhydrazone of formaldehyde (m.p. 163°) could not be detected.

6-*Formyl*-1:2-*chromene*.—A mixture of chromene (0.6 g.), dimethylformamide (0.5 c.c.) and $POCl_3$ (0.6 c.c.) was heated on a water-bath for 4 hours. The dark viscous mass was cooled, treated with warm alkali and extracted with ether, leaving behind a tarry residue. On removing ether, the *aldehyde* was obtained as an oil, yielding a crystalline 2:4-dinitrophenylhydrazone which was recrystallised from acetic acid in ochreous needles, m.p. 266° (decomp.), depressed to 245° on admixture with the 2:4-dinitrophenylhydrazone of 2-methyl-3-formylcoumarone (m.p. 261°, decomp.). (Found: C, 56.4; H, 3.5; N, 16.9. $C_{16}H_{12}O_5N_4$ requires C, 56.5; H, 3.5; N, 16.5%).

6-*Methyl*-1:2-*chromene* was prepared as chromene by the pyrolysis of 5-methyl-2-(γ-hydroxypropenyl)-phenol as a colorless liquid, b.p. 185°/320 mm, $n_D^{31.5}$ 1.5737,

yield 30%. The *picrate* was crystallised in orange prisms from alcoholic picric acid, m.p. 55-56°.

5:6-*Benzo*-1:2-*chromene* was prepared as above from 1-(γ-hydroxypropenyl)-2-naphthol, but in a poor yield (10-15%), as a yellowish mobile liquid, b.p. 200°/3 mm. It developed a yellow colour with H_2SO_4, turning green on keeping. (Found: C, 85.1; H, 5.8. $C_{13}H_{10}O$ requires C, 85.7; H, 5.5%). The *picrate* was obtained as red needles, m.p. 116-17°.

7:8-*Benzo*-1:2-*chromene* was obtained by the pyrolysis of 2-(γ-hydroxypropenyl)-1-naphthol as a yellowish liquid, b.p. 140-45°/1mm (bath temperature). It developed a yellow coloration with H_2SO_4, turning green on keeping. (Found: C, 85.1; H, 5.8. $C_{13}H_{10}O$ requires C, 85.7; H, 5.5%). The *picrate* was obtained as red needles, m.p. 109-10°.

Chroman from 1:2-*Chromene*.—Chromene (0.9 g.) was catalytically reduced at the room temperature and atmospheric pressure with palladised charcoal in acetic acid when the theoretical amount of hydrogen was absorbed in 10 minutes. On working up, chroman was obtained as a colorless liquid (0.7 g.), b.p. 220°/750 mm; n_D^{26} 1.5307 (lit. for chroman: n_D^{22} 1.5440; for 2-methylcoumaran: n_D^{22} 1.5307). With H_2SO_4 it gave a yellowish brown colour, turning green quickly; 2-methylcoumaran under the same condition gave a yellowish brown colour.

6-*Formylchroman*.—A mixture of chroman (6.0 g), dimethylformamide (5 c.c.) and $POCl_3$ (7 c.c.) was heated on a water-bath for 8 hours. The mixture was then decomposed with water, made alkaline and extracted with ether. After removing the solvent, the liquid was distilled. After a short forerun (0.5 c.c.), the *aldehyde* was obtained as a colorless liquid, b.p. 160-63°/20 mm. (Found: C, 74.4; H, 6.3. $C_{10}H_{10}O_2$ requires C, 74.1; H, 6.2%). The 2:4-*dinitrophenylhydrazone* was obtained as orange-red needles, m.p. 255-56°. (Found: N, 15.9. $C_{16}H_{14}O_5N_4$ requires N, 16.4%). The *semicarbazone* separated from alcohol in colorless needles, m.p. 236° (decomp.).

6-*Methylchroman*.—The above aldehyde (3.0 g.) in purified diethyleneglycol (10 c.c.) was treated with hydrazine hydrate (3 c.c., 100%) when the mixture warmed up. KOH (4 g.) was added and the mixture was heated in an oil-bath at 180° with continuous removal of water and the reduced material. After 1 hour the mixture was worked up to afford 6-methylchroman (2.5 g.), b.p. 160-65°/115 mm, $n_D^{31.5}$ 1.5369, identical with an authentic specimen prepared according to Benneville and Connor (*loc. cit.*) from 6-methylcoumarin having $n_D^{31.5}$ 1.5369 (lit. 1.5392 at 25°).

2-*Methyl*-5-*formylcoumaran*.—A mixture of 2-methylcoumaran (1.0 g.), dimethylformamide (0.5 c.c.) and $POCl_3$ (1.5 c.c.) was heated on the water-bath for 4 hours. The deep brown solution on working up gave 2-*methyl*-5-*formylcoumaran* as a liquid (0.6 g.), characterised by 2:4-*dinitrophenylhydrazone*, which was crystallised from acetic acid in deep orange-red crystalline mass, m.p. 230°. (Found: N, 16.0. $C_{16}H_{14}O_5N_4$ requires N, 16.4%).

2-*Methyl*-4:5-*benzocoumarone*.—The azlactone (10 g.) from 2-methoxy-1-naphthaldehyde (Mauthner, *J. prakt. Chem.*, 1917, **95**, 55) was boiled under reflux with NaOH

(50 c.c., 10%) for 5 hours and then cooled. The yellowish precipitate separating was filtered, suspended in water and acidified with HCl (conc.). 2-Methoxy-1-naphthylpyruvic acid (4 g., m.p. 119-20°) was obtained contaminated with 2-methoxy-1 methylnaphthalene (cf. Mauthner, *loc. cit.*).

The *oxime* of the keto-acid was prepared by adding hydroxylamine hydrochloride (3 g.) in NaOH (60 c.c., 10%) to the pyruvic acid (3.8 g.) and leaving the mixture overnight. On acidification, the oxime (4.0 g.) was obtained, crystallising from alcohol in colorless powder, m.p. 168-69° (decomp.). (Found : N, 5.1. $C_{14}H_{13}O_4N$ requires N, 5.4%). On dehydration with acetic anhydride, the oxime gave 2 methoxy-1-naphthylacetonitrile (2.6 g.), crystallising from alcohol in colorless prisms, 113-14° (Cook *et al., J. Chem. Soc.*, 1941, 502, report m.p. 111° for the compound prepared by a different route). (Found : C, 79.3 ; H, 5.9. Calc. for $C_{13}H_{11}ON$: C, 79.2 ; H, 5.6%).

The cyanide (2.0 g.) was condensed with ethyl acetate (1.0 g.) in presence of sodium methoxide (from sodium, 0.4 g.) in benzene (15 c.c.) for 4 hours. The *sodium salt* of the resulting *keto-nitrile* separated and the mixture worked up as usual to furnish keto-nitrile as an uncrystallisable oil which was directly hydrolysed by boiling with acetic acid (5 c.c.) and HBr (6 c.c.) for 1½ hours. On cooling, the oil separating solidified. This was collected, washed with alkali and water, dried and crystallised from alcohol, affording *2-methyl-4 : 5-benzocoumarone* as colorless leaflets, m.p. 138-40°, yield 0.45 g. (Found : C, 85.6, 85.4 ; H, 5.0, 5.3. $C_{13}H_{10}O$ requires C, 85.7 ; H, 5.5%). The compound showed a bluish violet colour with H_2SO_4.

1-Methoxy-2-naphthaldehyde, m.p. 47°, was prepared from isatin and 1-naphthol by the laborious method of Friedländer (*loc. cit.*). The *2 : 4-dinitrophenylhydrazone* was crystallised from acetic acid in orange-red leaflets, m.p. 244°.

2-Methyl-6 : 7-benzocoumarone.—A mixture of the foregoing aldehyde (0.5 g.), hippuric acid (0.8 g.), fused sodium acetate (0.2 g.) and acetic anhydride (2 c.c.) was heated on a water-bath for 1 hour. On cooling, the mass solidified. This was treated with alcohol (5 c.c.) and the yellow crystals of the *azlactone* collected, washed with hot water and alcohol. This was crystallised from benzene in yellow needles (0.55 g.), m.p. 195°. (Found : N, 4.0. $C_{21}H_{15}O_3N$ requires N, 4.3%).

Hydrolysis.—A mixture of the azlactone (0.53 g.), hydrated baryta (1.5 g.), water (8 c.c.) and alcohol (2 c.c.) was refluxed for 18 hours and the *barium salt* separating was collected and washed with warm alcohol which removed 1-methoxy-2-methylnaphthalene. On acidification, the salt gave yellowish keto-acid which was directly converted into the *oxime*, m p. 170° (decomp.) as above, yield 0.21 g. (Found : N, 5.2. $C_{14}H_{13}O_4N$ requires N, 5.4%). The above alcoholic washings on evaporation afforded 1-methoxy-2-methylnaphthalene as an oil, characterised by its *picrate*, m.p. 95°, identical with an authentic sample as given below. (Found : N, 10.0. $C_{12}H_{12}O.C_6H_3O_7N_3$ requires N, 10 5%). The oxime (0.2 g.) on treatment with acetic anhydride (1 c.c.) gave *1-methoxy-2-naphthylacetonitrile* which was crystallised as colorless plates, m.p. 48-49° from petroleum ether, yield 0.14 g. (Found : C, 79.0 ; H, 5.4. $C_{13}H_{11}ON$ requires C, 79.2 ; H, 5.6%). The nitrile (135 mg.) was condensed with ethyl acetate (90.13 c.c.) in presence of sodium ethoxide (from sodium, 30 mg.) in benzene (3 c.c.)

for 3 hours. The gummy *keto-nitrile* (120 mg.), isolated as usual, was boiled with HBr (1 c.c., 48%) in acetic acid (1.5 c.c.) for 3 hours. After basification, the neutral matter was isolated with ether and was obtained as a solid. *2-Methyl-6 : 7-benzocoumarone* was crystallised from alcohol in colorless long needles (6 mg.), m.p. 234°, showing bluish violet colour with H_2SO_4. (Found : C, 85.3 ; H, 5.6. $C_{13}H_{10}O$ requires C, 85.7 ; H, 5.5%).

1-Methoxy-2-methylnaphthalene was prepared for comparison from 1-hydroxy-2-naphthaldehyde. The aldehyde (0.5 g.) was reduced with hydrazine hydrate (1 c.c., 100%), alkali (0.5 g.) and diethyleneglycol (4 c.c.) at 180° for 2 hours under the Huang-Minlon condition and then directly methylated, without isolation, with excess of methyl sulphate. Steam-distillation afforded 1-methoxy-2-methylnaphthalene as an oil (0.25 g.) (Tryon *et al.*, *J. Amer. Chem. Soc.*, 1948, **70**, 2004, report b.p. 129-30°/9 mm). The *picrate* was crystallised in orange needles, m.p. and mixed m.p. with above specimen, 95°. The *2 : 4 : 7-trinitrofluorenone derivative* separated from acetic acid in maroon needles, m.p. 162°.

Lithium Aluminium Hydride Reduction of 2-Hydroxy-1-naphthaldehyde or its Triacetyl Derivative.—The solution of the compound (1.0 g.) in ether (30 c.c.) was added with stirring to a slurry of $LiAlH_4$ (0.5 g.) in ether (50 c.c.) at 0°. After leaving for 1 hour, the mixture was decomposed with H_2SO_4 and worked up to provide *bis-2-hydroxy-1-naphthylmethane*, m.p. and mixed m.p. 201° ; yield 0.2 g. (Found : C, 83.7; H, 5.5. Calc. for $C_{21}H_{16}O_2$: C, 84.0 ; H, 5.5%). The identity was further confirmed by oxidation with alkaline hypobromite to dehydro-*bis*-(2-hydroxy-1 naphthyl)-methane, m.p. 170°.

cis-o-*Hydroxycinnamic Aldehyde.*—*cis-o*-Hydroxycinnamyl alcohol (0.5 g.) in chloroform (18 c.c.) was refluxed with pure MnO_2 (6 g.) for 15 hours and then worked up to furnish the *aldehyde* as an oil (0.2 g., Pauly and Wascher, *Ber.*, 1923, **56**, 603, report m.p. 133°, which may be a stereoisomeride). The compound developed a deep yellow colour with ferric chloride. The *2 : 4-dinitrophenylhydrazone* was crystallised from alcohol in deep orange-red plates, m.p. 257-59° (decomp.). (Found : C, 55.0 ; H, 3.7. $C_{15}H_{12}O_5N_4$ requires C, 54.9 ; H, 3.6%).

The author wishes to thank Mr. A. K. Mitra for carrying out preliminary experiments. Thanks are also due to Prof. B. P. Gyani and Principal M. Q. Doja for facilities.

CHEMICAL LABORATORY,
SCIENCE COLLEGE,
PATNA.

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THE SOLUBILITY AND AMPHOTERIC PROPERTIES OF MERCURIC OXIDE

By T. M. Salem

From the mean of ten determinations, the solubility and amphoteric properties of mercuric oxide have been examined. The solubility in water at 35° has been found to be 3.47×10^{-4} g. mol. Hg/litre. From solubility determinations in buffer solutions of varying *p*H and in alkali hydroxide, the isoelectric point of mercuric oxide has been found to lie between *p*H 7.5 and 8.0. A potentiometric method has been used for the determination of small amounts of mercury, using potassium iodide solution. The indicator electrode is an amalgamated platinum electrode. An amount of mercury as small as 0.5 mg /100 c.c. can be determined with an accuracy of not less than 1%.

In connection with a study of the behaviour of mercury as well as mercury-mercuric oxide electrodes in solutions of varying *p*H and initially containing no mercury ions (El Wakkad and Salem, *J. Phys. Coll. Chem.*, 1950, **54**, 1371 ; *J. Phys. Chem.*, 1952, **56**, 621), it appeared desirable to re-examine the solubility and amphoteric character of mercuric oxide.

Every hydroxide possesses in some measure both acidic and basic character (Kossel, *Ann. Physik*, 1916, **49**, 303 ; Laue, *Z. anorg. Chem.*, 1927, **165**, 325). The hydrogen-ion concentration for an ampholyte in regard to its acid and basic dissociation constants is given by the well-known relation :

$$[H^+] = \sqrt{K_a . K_w / K_b} .$$

The value of K_a (Garret and Howel, *J. Amer. Chem. Soc.*, 1939, **61**, 1730) for mercuric oxide for the reaction :

$$H_2HgO_2 \rightleftharpoons H^+ + H\,HgO_2^-$$

is $K_a = 1.4 \times 10^{-15}$ and the ion product is 3.4×10^{-19}, while the value of K_b for the reaction :

$$Hg(OH)_2 = Hg(OH)^+ + OH^-$$

is $K_b = 7.1 \times 10^{-12}$ and the ion product is 1.7×10^{-15}. This is an evidence of a nearly neutral hydroxide and with a minimum solubility, shifting slightly on the basic side.

Numerous investigations were carried out on the amphoteric character of mercuric oxide in order to elucidate the exact position of its isoelectric point (Cohen, *Z. physikal. Chem.*, 1900, **34**, 69 ; Hulett, *ibid.*, 1901, **37**, 385 ; Ostwald, *ibid.*, 1900, **34**, 495 ; Schich, *Amer. Chem. J.*, 1903, **29**, 321 ; Karl Schich, *Z. physikal. Chem.*, 1903, **42**, 155 ; Allmand, *Z. Elektrochem.*, 1910, **16**, 254 ; Kolthoff, *Chem. Weekblad*, 1914, **14**, 1016 ; Fuseya, *J. Amer. Chem. Soc.*, 1920, **42**, 368 ; Garrett and Hirshler, *ibid.*, 1938, **60**, 299 ; Garrett and Howel, *ibid.*, 1939, **61**, 1730), but none of these previous authors arrived exactly at the position of the minimum solubility.

Thus, it was considered desirable to know the exact position of the isoelectric point by measuring the solubility of mercuric oxide in pure water and in a wide range of concentrations of sodium hydroxide solutions and in buffer solutions of varying *p*H.

EXPERIMENTAL

Mercuric Oxide.—The red and yellow forms of mercuric oxide are similar in every respect save particle size (Ostwald and Schich, *Z. physikal. Chem.*, 1895, **17**, 183 ; 1895, **18**, 159 ; 1900, **34**, 495 ; Schich, *loc. cit.* ; Allmand, *loc. cit.* ; Frick, *Z. anorg. allgem. Chem* , 1927, **166**, 244 ; Zachariassen, *Z. physikal. Chem.*, 1927, **128**, 421). We prepared the red form possessing the larger particle size and the normal solubility. For this preparation a method similar to that of Garrett and Hirschler (*loc. cit.*) was followed. To get a nitrogen-free oxide, the sample was followed during the period of ignition with the micro-Kjeldahl method.

Sodium Hydroxide Solution.—From a saturated solution of Analar sodium hydroxide, kept in a Pyrex glass tube lined with paraffin wax for several days to allow carbonate to settle, the clear solution was transferred in an atmosphere of pure nitrogen to the dilution apparatus described by Vogel ("Quantitative Inorganic Analysis", Longmans Green and Co, London, 1939, p. 286). Dilutions prepared from this solution were standardised against hydrochloric acid. The concentration of these solutions varied from 0.500*M* to $3.68 \times 10^{-4}M$. The corresponding *p*H values covered a range from 10.22 to 13.19.

Buffer Solutions.—Buffer solutions of varying *p*H (7.05 to 9.11) were prepared according to Palitzsch (cited by Britton, "Hydrogen Ions", 2nd ed., Chapman and Hall, Ltd., London, 1932, p. 219). Solutions chosen have anions which would not form any compound with the oxide.

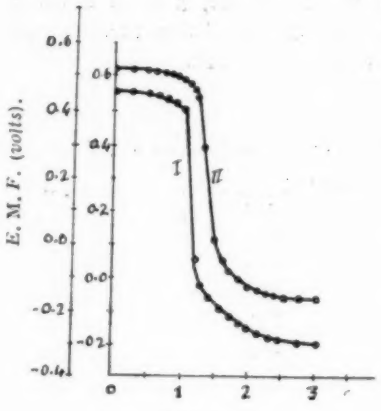
Conductivity Water.—Highly purified water was used in all our experiments. The water so prepared had a conductivity of 1×10^{-6} mhos.

Solubility Apparatus.—The prepared oxide was introduced under CO_2-free nitrogen into the steamed Pyrex flask of about 500 c.c. capacity with two side tubes- an inlet for nitrogen and an outlet. The gas was allowed to bubble through the solution for about five minutes before the two side tubes were sealed up. The flask was then agitated in a specially shaking device, similar in principle to Noyes' apparatus (*Z. physikal. Chem.*, 1892, **9**, 606). The samples were agitated for 120 hours at 50°. The temperature of the thermostat was then lowered to 35° and the process of agitation was continued for 2 days after which the samples were taken to sediment for 3 to 5 days in an air thermostat fixed at 35° ± 0.02°.

The clear solution was decanted in nitrogen atmosphere through a G 3 Jena sintered glass. A known volume of the filtrate was taken and analysed.

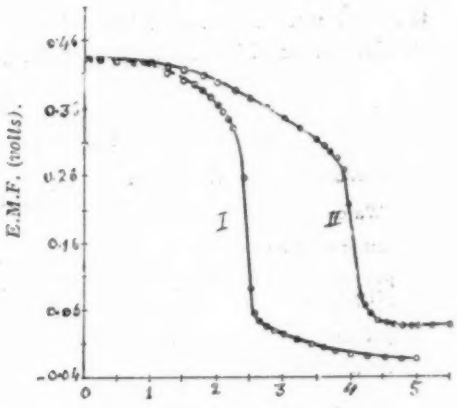
Analytical Procedure.—Comparatively little work has been done on the determination of mercury in solution (Marcip, *Bull. Soc. Chim. Belg.*, 1928, **37**, 241 ; Garrett and Hirschler, *loc. cit.* ; Garrett and Howel, *loc. cit.* ; Salem, Inst. D'Egypt, 1956, **2**, 38). A potentiometric method was used with an amount of mercury as small as 0.5 mg./100 c.c. with an accuracy involving an error of not more than 1%.

FIG. 1



I—4.72 × 10^{-2} g. Hg^{I} /100 c.c. vs. 0.188 *M*-KI
II—4.72 × 10^{-3} g. „ „ „ 0.0188 „

FIG. 2



I—6.9 × 10^{-4} g. Hg^{II}/100 c.c. vs. 0.0033 *M*-KI
II—1.32 × 10^{-3} g. „ „ „ „ „

A standard solution o $Hg(NO_3)_2$ was prepared by dissolving a weighed amount of mercury in nitric acid and diluting to a known volume. The mercurous stock solution was prepared from the purest B.D.H. $Hg_2(NO_3)_2$ of grade A.R. and was standardised according to Vogel ("Quantitative Inorganic Analysis", 2nd ed., Longmans Green & Co., 1951, p. 253). Potassium iodide was prepared from A.R. sample and conductivity water. The usual titration device was used in carrying out the experiments. A salt bridge of potassium nitrate—agar and a saturated calomel electrode as the reference half-cell were used throughout the measurements. The indicator electrode was an amalgamated platinum electrode prepared by electrolytic deposition using 3 m.a./electrode for 30 minutes from a dilute nitric acid solution, saturated with mercurous nitrate. The platinum cathode was 1 cm^2. Measurements were carried out in a thermostat at 35° ± 0.02° and were recorded on a Cambridge potentiometer. Some representative results are shown in Table I and Figs. 1 and 2 for the Hg^{I} and Hg^{II} solutions.

TABLE I

Amount of Hg^{I} in soln.	Conc. of KI soln.	Max. inflection per 0.1 c.c. of KI.	Hg found.	% Error.
0.11800 g.	0.188 *M*	273 mv	0.11900 g.	+0.8
0.04720	0.188	269	0.04700	−0.4
0.01180	0.0188	263	0.01192	+1.1
0.00472	0.0188	168	0.00470	−0.4
0.00118	0.00188	140	0.00119	+0.8
0.00047	0.00188	130	0.00047	±0.0
Amount of Hg^{II} in soln.				
0.06600	0.0332	85	0.06640	+0.6
0.00331	0.0033	192	0.00335	+1.2
0.00660	0.0032	150	0.00664	+0.6
0.00132	0.0033	105	0.00133	+0.7
0.00069	0.0033	170	0.00069	±0.0

For the analysis of the mercury content in the filtrate, a known volume was treated with 0.1*N*-H_2SO_4 to first colour change of methyl orange, 5 more drops of the acid were added and the solution was diluted to 150 c.c. before titration with standard 0.00298*M*-KI. Table II and Fig. 3 show the results obtained.

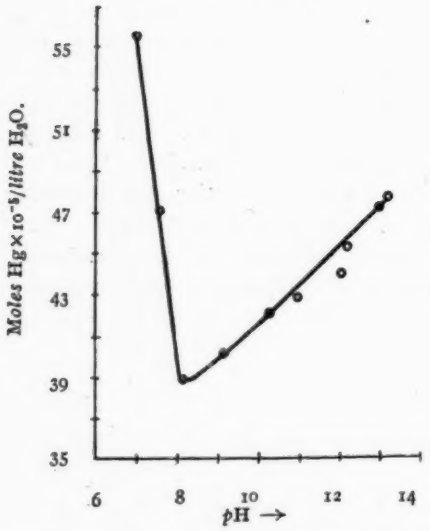
TABLE II

[100 c.c. of filtered solution titrated againgt $2.98 \times 10^{-3}M$ KI at 35°].

Solution.	KI soln. taken.	Solubility (g. Hg/litre).	Solubility (g. mols. Hg/litre × 10^{-4}).	*p*H.
Water	29.0 c.c.	0.0696	3.47	
Buffer solution :				
*p*H 7.05	37.2	0.1116	5.55	
*p*H 7.55	31.5	0.0945	4.71	
*p*H 8.09	26.0	0.0780	3.89	
*p*H 9.11	27.0	0.0810	4.03	
Alkali hydroxide solutions :				
$3.68 \times 10^{-4}N$	28.2	0.0850	4.23	10.22
2.06×10^{-3}	28.7	0.0860	4.28	10.96
3.19×10^{-3}	29.5	0.0885	4.40	12.08
5.00×10^{-3}	30.3	0.0910	4.53	12.24
2.65×10^{-1}	31.7	0.0941	4.73	12.94
3.00×10^{-1}	32.0	0.0960	4.78	13.19

Fig. 3 shows that the solubility of the mercuric oxide decreases and then increases with increase of alkali hydroxide concentrations. The isoelectric point of this oxide is between *p*H 7.5 and 8. At lower *p*H values the oxide in solution dissociates mainly as a base which may be $Hg(OH)_2$. At higher *p*H, the dissociation is mainly as an acid which may be H_2HgO. The minimum solubility is slightly on the basic side, confirming the prediction of Garrett and Howell, and of Fuseya (*loc. cit.*). The solubility in water is even less than that at *p*H 8.0. This is due to the oxide undergoing a dispersion into much finer particles when introduced into an alkali solution.

FIG. 3



From the foregoing results, it is clear that mercuric oxide possesses weak acid properties and that the isoelectric point should be on the alkaline side near the neutral point. The reaction expected should be accordingly :

$$H_2HgO_2 + OH^- = HHgO_2^- + H_2O.$$

CHEMISTRY DEPARTMENT,
UNIVERSITY COLLEGE FOR GIRLS,
AIN SHAMS UNIVERSITY,
HELIOPOLIS, CAIRO, EGYPT.

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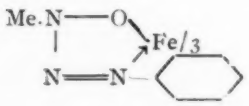
SPECTROPHOTOMETRIC DETERMINATION OF IRON WITH 3-HYDROXY-1-PHENYL-3-METHYLTRIAZINE

By H. K. L. Gupta and N. C. Sogani

Fe^{III} forms a greenish blue, water soluble complex with 3-hydroxy-1-phenyl-3-methyltriazine in the *p*H range from 3.1 to 4.5 with an absorption peak at 625 mμ. This reaction has been used for the direct spectrophotometric determination of iron in presence of almost all the commonly associated elements. The system obeys Beer's law in the concentration range of 1 to 10 p.p.m. of iron. The sensitivity of the colour reaction determined in Nessler's cylinders is 1 part of iron in 4,500,000 parts of solution and on spot plate is 0.1 γ of iron. The formula of the complex has been determined to be FeR_3 (R=reagent). The molecular extinction coefficient at 625 mμ and the dissociation constant at 34° have been determined to be 2.8×10^3 and 1.156×10^{-11} respectively, and the free energy of formation of the complex as −15.3 K cal./mole.

A new series of potentially useful analytical reagents has been reported by Sogani and Bhattacharyya (*Anal. Chem.*, 1956, **28**, 81, 1616). 3-Hydroxy-1:3-diphenyltriazine has been used successfully for the gravimetric estimation of copper, palladium and nickel and the derivative, 3-hydroxy-1-*p*-sulphonatophenyl-3-phenyltriazine, for the spectrophotometric determination of palladium (*ibid.*, 1957, **29**, 397) and molybdenum (this *Journal*, 1958, **35**, 842). These compounds possess common functional grouping -N(OH)-N=N-. In the present investigation an attempt has been made to study the analytical aspects of 3-hydroxy-1-phenyl-3-methyltriazine which has an identical chelating system, with the difference that the oxime group is attached to a methyl group in place of a phenyl group. This considerably reduces the acidic characteristics of the oxime group. Bamberger *et al.* (*Ber.*, 1897, **30**, 2283) have reported that this compound with ferric chloride develops an intense greenish blue colour. This property has been made use of successfully in the spectrophotometric determination of Fe^{III}. Fe^{II} does not exhibit any coloration. Almost all the commonly associated diverse ions do not interfere in the direct determination of iron. The formation of iron complex with the reagent is almost instantaneous and is stable for 40 minutes at 34°. Apart from other reasons, the fading of the colour with time is due to the reducing effect of the reagent which converts Fe^{III} to Fe^{II}.

The empirical formula of the complex, determined by applying Job's continuous variation method (*Ann. chim.*, 1928, *x*, **9**, 113) has been found to be FeR_3. It can be best represented by the following chelate structure:



EXPERIMENTAL

Bamberger *et al.* (*loc. cit.*) have described the preparation of 3-hydroxy-1-phenyl-3-methyltriazine by reducing nitromethane with phenylhydrazine. We have prepared it by allowing methylhydroxylamine to react with benzenediazonium chloride in acetate-buffered solution at 0°.

An aqueous solution of methylhydroxylamine, prepared by reducing 6.6 c.c. of nitromethane with zinc dust in ammonium chloride medium, was stirred mechanically with sufficient quantity of crushed ice to keep the temperature at 0°. A solution of benzenediazonium chloride, prepared from 4.6 c.c. of aniline, was then added slowly to the above solution under mechanical stirring. Small portions of a concentrated sodium acetate (20 g.) solution were added occasionally to prevent it from becoming too acidic and to maintain the *p*H at about 5.0. The compound was thrown out in the form of a white granular precipitate. It was filtered under suction, washed with ice-cold water and crystallised from warm water in the form of white needles, yield about 3 g , m p. 69.0° (lit. m.p. 69-70°, *loc. cit.*).

It is highly soluble in alcohol and alcohol-water mixtures. Its solubility in water at 34° is 0.458 g./100 g. of water. The solid compound as well as its solution is highly stable.

Standard Fe^{III} solution was prepared by oxidising 17.875 g. of ferrous ammonium sulphate (A.R.) with nitrtc acid and the volume was made to 1 litre. It was diluted to give a solution containing 100 p.p.m. of iron.

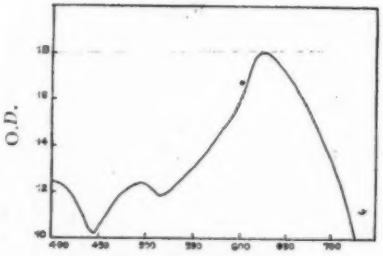
Reagent solution was prepared by dissovling 0.2 g. of the substance in about 2 c.c. of rectified spirit and making the volume to 100 c.c. with distilled water.

A Bausch and Lomb 'Spectronic-20' was used for measuring the absorption using 1 cm cuvettes. *p*H measurements were made with a Beckman *p*H meter (model, H-2). Visual colour comparisons were made with 50 c.c. Nessler's cylinders.

Spectral Characteristics of Iron Complex.—A standard iron solution (2 c.c.) containing 100 p.p.m. iron was taken in a 50 c.c. flask and a 0.25% sodium acetate solution (2.4 c.c.) was added so that the *p*H of the solution after dilution was about 3.5. The reagent solution (10 c.c.) was then added and the volume was made up to the mark. Absorption was measured at different wave-lengths from 390 to 800 mμ. As the reagent solution has no absorption in the visible range, water was used as a blank solution.

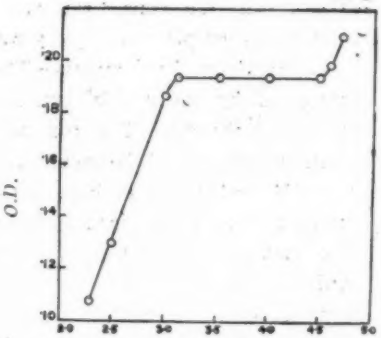
Fig. 1 shows the absorption curve of iron complex. It shows peaks at 400, 490 and 625 mμ. The optical density at 625 mμ is maximum, hence it was considered to be the most suitable wave-length at which all subsequent measurements were made.

FIG. 1



Iron complex (4 p.p.m.)

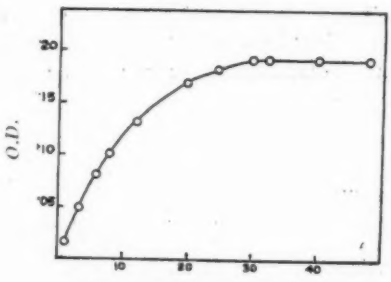
FIG. 2



Effect of pH.—Solutions containing the same concentrations of iron and the reagent were prepared at different *p*H values and absorption was measured at 625 mμ. The range of constant maximum absorption has been found to be between *p*H 3.1 and 4.5 (Fig. 2). Below *p*H 3.0 the solutions are coloured blue, between *p*H 3.1 and 4.5, greenish blue and above *p*H 4.5, they are violet with slight turbidity. This is indicative of iron complexes of different compositions at different H^+-ion concentrations.

Reagent Concentration and Mole Ratio.—Solutions containing the same concentrations of iron and different quantities of the reagent were prepared at *p*H 3.5 to 3.7 and the optical densities measured at 625 mμ. Fig. 3 shows the effect of increase of moles of the reagent per mole of iron on optical density. There is a very gradual rise in absorbance, indicating that the complex is in a highly dissociated form in solution. Full development of colour is ensured at 1:30 ratio of iron to the reagent.

FIG. 3



Rate of Reaction and Stability of Complex.—The full colour development of the iron complex is almost instantaneous and it is stable afterwards for 40 minutes.

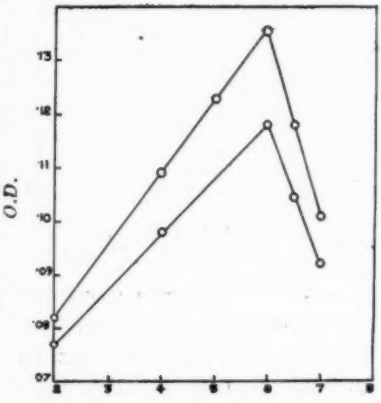
Effect of Temperature on the Reaction.—The colour intensity of iron complex was slightly decreased with the increase in temperature. There was no difference in the absorption at 25° and 35°. Hence, maintaining the temperature within 10° is considered desirable.

Beer's Law.—Beer's law was obeyed in the concentration range of 1 to 10 p.p.m. of iron. At higher concentrations of iron a slight turbidity occurs. The molecular extinction coefficient of the iron complex at 625 mμ has been found to be 2.8×10^3.

Sensitivity of Reaction.—Sensitivity of the reaction was determined in Nessler's cylinders in the usual way and was found to be 1 of iron in 4,500,000 parts of solution. Spot plate sensitivity was found to be 0.1γ of iron.

Formula of the Complex.—The molar composition of the iron complex was investigated by using Job's method of continuous variation (*loc. cit.*). The iron content of the final solution was varied between 7.12×10^{-5} and $5.69 \times 10^{-6} M$ and *p*H was kept at about 3.5. Fig. 4 shows the curves obtained by applying this method. The maxima at 6 c.c. of the reagent to 2 c.c. of equimolar iron indicates the ratio of iron to reagent as 1 : 3. It is likely that different colours of iron complexes below *p*H 3.0 and above *p*H 4.5 are indicative of complexes of different compositions. But because of their unstable nature, spectrophotometric methods for studying their compositions could not be applied.

FIG. 4



x c c reagent added to (8-x) c.c. of equimolar iron.

Tolerance of Diverse Ions.—The tolerance of diverse ions was studied in the usual manner. Table I records the results obtained.

Qualitative spot plate testing has shown that Pb^{2+}, Sn^{2+}, Hg^{2+}, Sb^{3+}, Bi^{3+}, Cd^{2+}, Ti^{4+}, Ce^{4+}, ZrO_2^{2+}, VO_2^{2+}, Th^{4+}, V^{3+}, Pt^{4+}, and alkali and alkaline earth metals and common anions do not give any colour reactions with the reagent and are not likely to interfere in the spectrophotometric determination of iron. Ag^{+} and Au^{3+} are slowly reduced by the reagent. Phosphate and tartrate interfere. Copper gives a slight precipitate with the reagent. Determination of iron can be made by filtering out the copper precipitate from the solution.

TABLE I

Fe^{3+} = 4 p.p.m.

Ion.	Added as.	Conc. of ion (p.p.m.).	Ion.	Added as.	Conc. of ion (p p.m.).
Co^{2+}	Sulphate	100	Al^{3+}	Sulphate	100
Ni^{2+}	,,	100	Cr^{3+}	,,	20
Zn^{2+}	,,	100	MoO_4^{2-}	Sodium	10
Mn^{2+}	Chloride	100	WO_4^{2-}	,,	30
Cu^{2+}	Sulphate	50	Ca^{2+}	Chloride	100
Fe^{2+}	,,	100			

DISCUSSION

The dissociation of the complex in solution can be written as :

FeR_3	$\rightleftharpoons$	Fe +	$3R$	
C		0	0	(Initial conc.)
$(1-\alpha)C$		αC	$3\alpha C$	(Final conc.)

α being the degree of dissociation and C, the concentration of the complex, assuming no dissociation. The dissociation constant K is given by the equation :

$$K = \frac{\alpha C \times (3\alpha C)^3}{C(1-\alpha)} = \frac{27\,\alpha^4 C^3}{1-\alpha}.$$

The value of α may be obtained from Fig. 3 by the following relationship :

$$\alpha = \frac{E_m - E_s}{E_m} = \frac{0.194 - 0.05}{0.194} = 0.74,$$

where E_m is the maximum absorption obtained from the horizontal portion of the curve, when all the iron is present in the form of complex and E_s is the observed absorption at the stoichiometric molar ratio of the reagent to iron in the complex (Harvey and Manning, *J. Amer. Chem., Soc.*, 1950, **72**, 4488). The concentration, C, of the complex is equal to the total concentration of iron which is $7.16 \times 10^{-5} M$. By substituting these values in the above equation, the value of K at 34° comes to 1.156×10^{-11}. Hence, the stability constant K' of the complex is equal to 8.65×10^{10}.

The standard free energy of formation of the complex from iron sulphate and 3-hydroxy-1-phenyl-3-methyltriazine is calculated from the relation $\Delta F^\circ = RT \ln K$ and works out to be -15.3 K cal./mole at 34°.

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CHEMISTRY DEPARTMENT,
GOVERNMENT COLLEGE,
AJMER.

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TRITERPENE COMPOSITION OF *LEUCONOTIS EUGENIFOLIA* DC.*

By Mrs. A. Chatterjee, B. Das and S. K. Roy

The stem of *Leuconotis eugenifolia* DC. contains alkaloids which have not been encountered in the leaves. The latter, however, show the presence of several terpenoids from which lupeol acetate and a new sapogenol, designated as leuconol, $C_{30}H_{50}O$, have been isolated. The physical and chemical properties of leuconol have been studied. It contains a hydroxyl group and an unsaturation which is found to be reluctant to catalytic hydrogenation

Under the research programme on the systematic survey of Apocynaceous plants, which are highly rich in alkaloids and terpenoid compounds, it was felt desirable to examine *Leuconotis eugenifolia* DC. This species grows luxuriantly in Indonesia.

A generous supply of this plant material was made available to the present authors through the kind co operation of Mr. N. G. Bisset, Treub Laboratory, Bogor, Indonesia. The stem of *L. eugenifolia*, when processed in the customary manner for alkaloidal compounds, gave positive tests for alkaloids. The isolation and characterisation of the alkaloids are in progress, the details of which will be reported in subsequent communications.

In the leaves, however, alkaloids have been found absent, but several triterpenoids have been isolated from which lupeol acetate (m.p. 215-16°, yield 0.00017%)) and a new sapogenol (m.p. 214-15°, yield 0.0017%) have been obtained in pure states from the neutral terpenoid fraction. Since the sapogenol appears to be a new compound, as evidenced from its properties and optical rotation, it has been named leuconol.

Leuconol, $C_{30}H_{50}O$, is fairly soluble in benzene, chloroform, petroleum ether (b.p. 60-80°) and moderately soluble in acetone, methyl alcohol and ethyl alcohol. It crystallises in shining needles from a mixture of benzene and ethyl alcohol or from chloroform and acetone. It produces a yellow coloration with tetranitromethane in chloroform, showing the presence of unsaturation but it is not amenable to catalytic hydrogenation. Leuconol is optically active and *dextro*-rotatory, $[\alpha]_D^{28\cdot5} + 53°.9$. The oxygen function of this sapogenol has been easily characterised as hydroxyl since it forms a monoacetate, $C_{32}H_{52}O_2$, m.p. 211-12°, and a monobenzoate, $C_{37}H_{54}O_2$, m.p. 224°. Further work on the structure-proof of leuconol is under progress.

Experimental

Dry and milled leaves of *Leuconotis eugenifolia* DC. (300 g.) were extracted with alcohol (3 litres) for 15 days at room temperature. The alcohol extract was concentrated in vacuo on a steam-bath. The dark green residue was poured into water contain-

* LIII. Communication in the series, "Studies on terpenoids, coumarins and alkaloids of Medicinal plants".

ing 1% acetic acid (100 c.c.) when a solid mass, adherent with a large amount of chlorophyll, separated out. It was filtered and dried (yield 15 g.) A portion of the solid (3 g.) was dissolved in rectified spirit, charcoalised to remove chlorophyll and filtered. The filtrate was concentrated in vacuo over a water-bath and the yellow residue was taken up in ether. The ether solution (A) was washed with 2% aqueous potassium hydroxide (50 c.c.) to separate the phenolic and acidic constituents, if any. The alkaline extract was acidified with HCl (conc.) and extracted with ether. The ether extract was washed with water, dried over anhydrous sodium sulphate and concentrated when a solid (yield 0.2 g.) was obtained which did not respond to the Liebermann-Burchard test. Attempts to crystallise this substance from different solvents were not successful.

The ether solution (A) was washed with water, dried over anhydrous sodium sulphate and concentrated. The residue (1.2 g.) responded to the Liebermann-Burchard colour reaction. The solid was dissolved in benzene (30 c.c.) and subjected to chromatographic resolution over Brockmann alumina (35 cm × 2.5 cm). The chromatogram was developed with petroleum ether (b.p. 60-80°), then with a mixture of the same solvent and benzene in various proportions and finally with benzene. Eluents were collected in fractions of 30 c.c. each (Table I).

TABLE I

Eluents.	Fractions collected.	Residue.
Petroleum ether (b.p. 60-80°)	1-5	Nil
Do	6-7	Solid, m.p. 190-204°
Do	8-10	Nil
Petroleum ether (b.p. 60-80°) and benzene (1 : 1)	11-15	Solid (non-crystallisable)
Do	16-19	Solid, m.p. 165-72°
Do	20-24	Solid, m.p. 170-77°
Do	25-30	Solid, m.p. 175-80°
Do	31-32	Nil
Petroleum ether (b.p. 60-80°) and benzene (1 : 2)	33-38	Nil
Benzene	39-41	Nil

Isolation of Lupeol Acetate.—Fractions (6-7) were crystallised from acetone in fine needles, m.p. 215-16°, yield 0.05 g. (Found in a sample dried over P_2O_5 in vacuo: C, 82.32 ; H, 11.54. Calc. for $C_{32}H_{52}O_2$: C, 82.05 ; H, 11.11%). The melting point of the compound remained unchanged on admixture with an authentic sample of lupeol acetate.

Isolation of a New Triterpene Alcohol, Leuconol.—Fractions (16-30) were combined and subjected to chromatographic resolution over Brockmann alumina (30 cm × 2.5 cm). The chromatogram was developed as before (*vide supra*). Eluents were collected in fractions of 25 c.c. each (Table II).

TABLE II

Eluents.	Fractions collected.	Residue.
Petroleum ether (b.p. 60-80°)	1-5	Nil
Petroleum ether (b.p. 60-80°) and benzene (1:1)	6-12	Nil
Do	13-22	Solid, m.p. 180-85°
Do	23-30	Solid, m.p. 193-90°
Do	31-33	Nil
Petroleum ether (b.p. 60-80°) and benzene (1 :2)	34-36	Nil
Benzene	37-40	Nil

Fractions (13-30) on repeated crystallisations from a mixture of benzene and ethyl alcohol yielded fine needles, m.p. 214-15°, yield 0.5 g., $[\alpha]_D^{33\cdot5}$ + 53°.9 (in chloroform). (Found in a sample dried dover P_2O_5 in vacuo: C, 84.38; H, 11.97. $C_{30}H_{50}O$ requires C, 84.50; H, 11.73%). The compound developed a yellow colour with tetranitromethane, showing the presence of unsaturation in the molecule which, however, could not be reduced catalytically with PtO_2 in alcohol.

Monoacetyl-leuconol.—Leuconol (0.2 g.) was heated with acetic anhydride (1.0 c.c.) and three drops of pyridine on a water-bath for 4 hours. The reaction mixture was cooled and added to crushed ice and kept overnight in the cold. The solid separating was filtered, washed with water, dried and crystallised in colorless needles from acetone, m.p. 211-12°, yield 0.06 g. (Found in a sample dried over P_2O_5 in vacuo: C, 82.25; H, 11.36. $C_{32}H_{52}O_2$ requires C, 82.05; H, 11 11%).

Monobenzoyl-leuconol.—Leuconol (0.2 g.) was mixed with benzoyl chloride (1.0 c.c.) and 3 drops of dry pyridine and the mixture was heated on the water-bath for 4 hours. The reaction product was cooled, added to crushed ice and kept overnight in cold. The solid separating was filtered, washed with 2% aqueous KOH solution till free of benzoic acid, and finally with water and dried. The product was crystallised from acetone in needles, m.p. 224°, yield 0.04 g. (Found in a sample dried over P_2O_5 in vacuo: C, 83.79; H, 10.17. $C_{37}H_{54}O_2$ requires C, 83.77; H, 10.18%).

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DEPARTMENT OF ORGANIC CHEMISTRY,
UNIVERSITY COLLEGE OF SCIENCE
AND TECHNOLOGY, CALCUTTA.

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CHEMISTRY OF SOME ALKYLAMMONIUM ETHYLXANTHATES

By C. N. V. Nambury

Ethyl-, benzyl-, diethyl- and dimethyl-amine salts of ethylxanthic acid (EtO.CS.SH) have been prepared. In aqueous solutions of the respective amines or in presence of lead oxide in ether these afford the corresponding thiourethanes (R_2N CS OEt). On dry decomposition, related amine salts of appropriate dithiocarbamic acid (R_2N CS.SH_2NR_2) are formed which in the case of primary amine derivatives decompose further into the corresponding *s*-dialkylthiocarbamides (RNH.CS.NHR).

In the interaction of potassium alkyl xanthates with ethyl- and dimethyl- amines in an aqueous medium, leading to the corresponding thiourethanes, formation of amine-xanthates was envisaged as an intermediary stage (Nambury, *J. Vk. Univ.*, 1958, **2**, 101). Since the amine-xanthates do not appear to have been described earlier, preparation of a few of these compounds and a study of their properties are not without interest. By the direct interaction of ethylxanthic acid with ethyl-, diethyl-, dimethyl- and benzyl-amines in benzene medium, the related amine-xanthates have been now obtained :

$$(i)\quad EtO.CS.SH + R_2NH \longrightarrow EtO.C\overset{-}{S}.\overset{+}{S}\,NH_2R_2$$

(where R is an alkyl group or hydrogen).

These compounds are not very stable and deteriorate rapidly on storage, especially if moisture is not excluded. In aqueous solutions of the respective amines, and more rapidly in presence of finely divided yellow lead oxide, these (excepting diethylammonium ethylxanthate under former conditions) give rise to alkylthiourethanes :

$$(i)\quad R_2\overset{+}{N}H_2\overset{-}{S}.CS.OEt + PbO \longrightarrow R_2N.CS.OEt + PbS + H_2O$$

$$(ii)\quad R_2\overset{+}{N}H_2\overset{-}{S}.CS\,OEt + R_2NH \longrightarrow R_2N.CS.OEt + (R_2NH_2)\overset{+}{}\,\overset{-}{S}H,$$

thus, conclusively proving their role in the formation of thiourethanes, as reported earlier (*loc. cit.*).

On dry heating near their melting points, these decompose rapidly into the amine salts of the related dithiocarbamic acids, carbon disulphide and ethyl alcohol. Thus :

$$(iv)\quad 2R_2\overset{+}{N}H_2\overset{-}{S}.CS.OEt \longrightarrow CS_2 + EtOH + R_2N.C\overset{-}{S}.\overset{+}{H_2}NR_2.$$

In the case of ethylxanthates of primary amines (e.g., ethylamine and benzylamine), however, the reaction does not stop at the amine dithiocarbamate stage, but proceeds further, leading to the corresponding *s*-dialkylthiocarbamides (cf. Hofmann, *Ber.*, 1868, **1**, 25) :

$$RNH.C\overset{-}{S}.\overset{+}{H_2}NR \longrightarrow RNH.CS.NHR + H_2S.$$

It is interesting to note that formation of thiourethanes is completely excluded when dry salts are pyrolysed, and any considerable formation of dithiocarbamates or *s*-dialkylthiocarbamides does not occur in an aqueous medium where thiourethanes are the sole products.

Experimental

Ethyl-, benzyl-, diethyl- and dimethyl-amine salts of ethylxanthic acid were prepared as follows.

A benzene solution of ethylxanthic acid was obtained by the action of HCl (dil.) on cold (5°) aqueous solution of potassium ethylxanthate in presence of benzene (Zeise, *Ann. phys.*, 1835, **35**, 501). This on treatment with excess of the required amine, also in benzene, precipitated the corresponding amine-xanthate. It was collected, dried and allowed to stand in a vacuum desiccator. In each case, *s*-benzyl*iso*-thiuronium salt was prepared; mixed m.p. with authentic samples (Nambury, this *Journal*, 1957, **34**, 909), where no depression was observed, indicated that all the compounds were salts of ethylxanthic acid. On treatment with alkali, respective free amines were liberated. Nitrogen was estimated by Kjeldahl's method. The results of these experiments are summarised in Table I.

Table I

Salts of ethylxanthate.	M.P.	*s*-Benzyl*iso*thiuronium derivative, M.P.	% Nitrogen. Found.	Calc.
1. Ethylammonium- ($C_5H_{13}ONS_2$)	106°	98°	8.96	8.38
2. Diethylammonium- ($C_7H_{17}ONS_2$)	79-81°	97-98°	8.31	7.18
3. Dimethylammonium- ($C_5H_{13}ONS_2$)	95-99°	97°	9.50	8.38
4. Benzylammonium- ($C_{10}H_{15}ONS_2$)	97-99°	98°	6.19	6.12

Action of Lead Oxide on Amine-xanthates: Formation of Thiourethanes

Diethylammonium ethylxanthate (7 g.) was added with shaking to a suspension of finely powdered yellow lead oxide (20 g.) in ether (50 c.c.). The solid within a few minutes turned brown and finally black. The mixture on keeping overnight was filtered and the black residue rejected after repeated washing with ether. The ethereal filtrate on distillation afforded a liquid, b.p. 218°, identified with diethylthiourethane by estimation of nitrogen and comparing the properties with an authentic sample (Wheeler and Dustin, *Amer. Chem. J.*, 1900, **24**, 435). (Found: N, 8.44. Calc. for $C_7H_{15}ONS$: N, 8.69%).

Dimethylammonium ethylxanthate (3 g.) on similar treatment with lead oxide (15 g.) in moist ether (50 c.c.) gave dimethylthiourethane (2 c.c.), b.p. 203° (Nambury, *loc. cit.*, 1958).

Benzylammonium ethylxanthate (7 g.), when treated with lead oxide (20 g.) in moist ether (50 c.c.), afforded a liquid (2.5 c.c.), b.p. 180°/8 mm, and it was identified with benzylthiourethane through its sodium derivative (cf. Nambury, *loc. cit.*, 1958). The molecular weight was found to be 208 (calc. for $C_{10}H_{12}ONSNa$: 217).

Ethylthiourethane (2.8 c.c.) was analogously obtained by the action of lead oxide (15 g.) on ethylammonium ethylxanthate (5 g.) in ether, b.p. 205-208° (Hofmann, *Ber.*, 1869, **2**, 117).

Action of Aqueous Dimethylamine on Dimethylammonium Ethylxanthate.— Dimethylammonium ethylxanthate (2 g.), dissolved in minimum amount of water, was mixed with 30% aqueous dimethylamine (2 c.c.) with immediate formation of oily drops. After keeping overnight the oily liquid was extracted with ether and the extract evaporated after drying over fused calcium chloride. Distillation of the residual liquid furnished 1.2 c.c. of dimethylthiourethane, b.p. 203°.

A solution of dimethylammonium ethylxanthate (2 g.) in water (10 c.c.) was kept corked for several days. The solution remained clear, showing that the formation of dimethylthiourethane did not take place.

Dry Decomposition of Alkyl- and Aryl- ammonium Ethylxanthates at M.P. : Formation of Dithiocarbamates

Diethylammonium ethylxanthate (2 g.), when gently heated at its m.p., afforded a small quantity of a liquid, b.p. 50-80° and another fraction, b.p. 124°, which solidified to fine white crystals, m.p. 79-81°. The fraction of b.p. 50-80° was found to be a mixture of carbon disulphide and ethyl alcohol. The product, b.p. 124° (m.p. 79-81°), was identified with diethylammonium diethyldithiocarbamate.

Dimethylammonium ethylxanthate on similar treatment first gave a low boiling liquid (b.p. 50-80°) which also proved to be a mixture of carbon disulphide and ethyl alcohol. A second fraction distilled out at 137-40° and solidified to white crystals, m.p. 132°, identified with dimethylammonium dimethyldithiocarbamate.

Ethylammonium ethylxanthate (2.5 g.), when similarly heated (5 mins.), gave a mixture of carbon disulphide and alcohol, b.p. 50-80°, as in the above cases. The liquid residue in the flask, on cooling, gave crystals (0.9 g.), which, when washed with ether, melted at 103° and were identified with ethylammonium ethyldithiocarbamate (Hofmann, *loc. cit.*, 1868).

On heating for a longer duration (about 50 mins.), until the evolution of hydrogen sulphide had ceased, the product on crystallisation from water gave crystals, m.p. 70-74°. This was *NN'*-diethylthiocarbamide, formed by the decomposition of the dithiocarbamate (Hofmann, *loc. cit.*).

Benzylammonium ethylxanthate (3 g.), when heated on a water-bath for 10 minutes, gave, as in other cases, a mixture of carbon disulphide and alcohol (b.p. 50-80°). The residue in the flask on cooling gave a solid which was crystallised from absolute alcohol. The first crop of crystals (0.7 g.) on recrystallisation from methyl alcohol gave plates (m.p. 135°) which were identified with benzylammonium benzyldithiocarbamate. The absolute alcoholic mother-liquor, on evaporation and crystallisation of the residue, gave shining crystals, m.p. 148°, which were identified with *NN'*-dibenzylthiocarbamide.

Benzylammonium ethylxanthate (3 g.), on heating for a longer duration until no more hydrogen sulphide was evolved, gave a product which on crystallisation from alcohol afforded 1.0 g. of *NN'*-dibenzylthiocarbamide. No dithiocarbamate could be isolated in this experiment.

Pyrolysis of Benzylammonium Benzyldithiocarbamate at 130°.—Benzylammonium benzyldithiocarbamate (4.4 g.) was heated at 130° for 50 minutes. Evolution of hydrogen sulphide was observed. The solid product left behind (3.7 g., m.p. 139-46°) on crystallisation from absolute alcohol furnished shining crystals, m.p. 148° of *NN'*-dibenzylthiocarbamide.* The yield of dibenzylthiocarbamide corresponds to 91%.

Decomposition of Diethylammonium Ethylxanthate on Storage.—A sample of diethylammonium ethylxanthate (nearly 7-8 g.), when left for two weeks, turned brown and formed an oily liquid with a thiourethane smell. On extraction with ether it gave a residue of diethylammonium diethyldithiocarbamate, and on evaporation of the ether, 2.3 c.c. of a liquid of b.p. 205-208°, which proved to be diethylthiourethane.

Dimethylammonium ethylxanthate behaved similarly, affording a mixture of dimethylammonium dimethyldithiocarbamate and dimethylthiourethane.

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CHEMISTRY DEPARTMENT,
COLLEGE OF SCIENCE,
BENARAS HINDU UNIVERSITY,
VARANASI.

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*The various products obtained were identified by the technique of the melting points of mixtures with authentic samples and other characteristic reactions.

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STUDIES IN FRIEDEL-CRAFTS' ACYLATION. PART III. ACYLATION OF CHLORINE-SUBSTITUTED ANILIDE DERIVATIVES

By V. K. Mehta and S. R. Patel*

Friedel-Crafts' acylation of isomeric chloroacetanilides and chloroaceto-*o*-toluidides has been studied. In the case of *p*-chloroacetanilide and 4-chloro-6-methylacetanilide the reaction fails. The acylation of *m*-chloroacetanilide with acetyl chloride and of 3-chloro-6-methylacetanilide with chloroacetyl chloride afford the corresponding *p*-aminoketone, while that of *o*-chloroacetanilide with chloroacetyl chloride yields the corresponding *m*-aminoketone.

Kunckell *et al.* (*Ber. deut. Pharm. Ges.*, 1911, **21**, 419; *Chem. Zentrl*, 1912, I, 136; *Ber.*, 1900, **33**, 2641) studied the Friedel-Crafts acylation of acetanilide derivatives and reported that for the acylation to succeed, the acid halide should be chlorinated or should have a boiling point higher than 90°. Patel and coworkers (this *Journal*, 1956, **33**, 129, 867) have reported that it is possible to effect Friedel-Crafts' acylation of acetanilide and of *o*- and *m*-acetotoluidides with acetyl chloride if the reactants, viz., the anilide derivative, acetyl chloride and finely powdered anhydrous aluminium chloride, are heated in absence of any solvent in the proportion of 1 : 1 : 3 by weight respectively. The Friedel-Crafts acylation of acetotoluidides an anisidides with various acid halides has been reported (Buu-Hoï, Eckert and Royer, *Compt. rend.*, 1951, **233**, 627). Friedel-Crafts' acylation of the isomeric chloroacetanilides, except that of *m*-chloroacetanilide with chloroacetyl chloride (Kunckell and Richartz, *Ber.*, 1907, **40**, 3394), has not been reported so far. Hence, the study of the Friedel-Crafts acylation of chlorine-substituted acetanilide derivatives was undertaken.

Friedel-Crafts' acylation of *m*-chloroacetanilide with benzoyl chloride failed while that with acetyl chloride proceeded successfully, effecting substitution at *para* with respect to the acetamino group, the product formed being 2-chloro-4-acetaminoacetophenone (I). The constitution assigned to (I) has been proved by oxidising (I) with neutral permanganate to 2-chloro-4-acetaminobenzoic acid (II), m.p. 207°; the latter on hydrolysis yields 2-chloro-4-aminobenzoic acid (III), m.p. 213° (decomp.). Kunckell and Richartz (*loc. cit.*), who obtained (II) and (III) on oxidation of ω-2 dichloro-4-acetaminoacetophenone, reported the same melting point. For further confirmation, (III) has been converted into 2 : 4-dichlorobenzoic acid.

Friedel-Crafts' acylation of *o*-chloroacetanilide with acetyl chloride and also with benzoyl chloride failed, while with chloroacetyl chloride, the acylation proceeding successfully afforded ω-4-dichloro-3-acetaminoacetophenone (IV) in excellent yield. To prove the structure assigned to (IV), it was oxidised by neutral permanganate to 3-acetamino-4-chlorobenzoic acid (V), m.p. 263-64°. For the purpose of comparison and mixed m.p., (V) was synthesised by an alternate method consisting of reduction of 3-nitro-4-chlorobenzoic acid and subsequent treatment of the base formed with acetic anhydride (Bamberger, *Ber.*, 1902, **35**, 3708). Formation of (IV) suggests that Friedel-Crafts' acylation of *o*-chloroacetanilide with chloroacetyl chloride occurs in a

* Present address: B. D. College, Ahmedabad-1.

position *meta* with respect to the acetamino group. If the acylation had occurred in a position *para* with respect to the acetamino group, the product formed would have been ω-3-dichloro-4-acetaminoacetophenone, and this on oxidation would have afforded 4-acetamino-3-chlorobenzoic acid (VI).

(VI), synthesised by oxidation of 3-chloro-4-acetaminotoluene (VII) (Reverdin and Crepieux, *Ber.*, 1900, **33**, 2506) is different from (V) as it melts at 230-31°, and depresses the melting point of (V) on admixture. It would be interesting to note that Friedel-Crafts' acetylation of aceto-*o*-toluidide also occurs similarly in a position *meta* to the acetamino group (Sacha and Patel, this *Journal*, *loc. cit.*).

Friedel-Crafts' acylation of *p*-chloroacetanilide and of 4-chloro-6-methylacetanilide with acetyl chloride, benzoyl chloride and even with chloroacetyl chloride did not succeed, while that of 3-chloro-6-methylacetanilide with chloroacetyl chloride alone succeeded. The ketone formed has been assigned the constitution ω-2-dichloro-5-methyl-4-acetaminoacetophenone (VIII), which is supported on the basis that: (*a*) (VIII) on fusion with alkali does not furnish the indigo derivative, indicating that it is not an *ortho*-amino-ω-chloroacetophenone (Kunckell, *Ber.*, 1901, **34**, 124), and (*b*) the monobasic acid (IX), m.p. 306-308° (decomp.), obtained on oxidation of (VIII) on Ullmann's condensation with aniline, affords the corresponding diphenylamine-2-carboxylic acid, suggesting thereby that the (IX) is an *o*-halogeno-benzoic acid. This is possible if the constitution assigned to (VIII) is correct.

EXPERIMENTAL

Friedel-Crafts' Acetylation of m-*Chloroacetanilide with Acetyl Chloride*

2-*Chloro-4-Acetaminoacetophenone* (I).—To a mixture of *m*-chloroacetanilide (10 g.) and finely powdered anhydrous aluminium chloride (30 g.), kept cool in an ice-water bath, acetyl chloride (10 g.) was added in about four lots. The reaction mixture was stirred well after each addition, and then allowed to stand at room temperature for about an hour. It was then heated on a boiling water-bath for 3 hours. The cooled reaction mixture was decomposed with ice and HCl and the product (I) obtained was collected, washed and crystallised from boiling water in white tiny needles, m.p. 109-10°, yield 4 g. (Found: N, 6.76; Cl, 16.63. $C_{10}H_{10}O_2NCl$ requires N, 6.6; Cl, 16.8%).

2-*Chloro-4-aminoacetophenone*, obtained on hydrolysis of (I) with hot HCl (conc.), was crystallised from petrol-ether in small white shining prisms, m.p. 64-65°. (Found: N, 8.1; Cl, 20.8. C_8H_8ONCl requires N, 8.3; Cl, 20.9%).

N-*Benzoyl derivative*, obtained from the above base on treating it with excess of benzoyl chloride in alkali solution, was crystallised from dilute alcohol in small shining needles, m.p. 115-16°. (Found: N, 5.0; Cl, 12.8. $C_{15}H_{12}O_2NCl$ requires N, 5.1; Cl, 13.0%).

2 *Chloro-4-acetaminobenzoic Acid* (II).—A mixture of (I, 2 g.), 3% $KMnO_4$ solution (100 c.c.) and magnesium sulphate (5 g.) was heated on a boiling water-bath till the permanganate colour disappeared, and filtered hot. The filtrate was evaporated to half its bulk, cooled and just acidified. The product (II), which

separated as a white light solid, was crystallised from boiling water in white needles, m.p. 207° (Kunckell and Richartz, *Ber.*, 1907, **40**, 3395). (Found: Equiv., 209.0; N, 6.4; Cl, 16.7. Calc. for $C_9H_8O_3NCl$: Equiv., 213.5; N, 6.6; Cl, 16.6%).

2-Chloro-4-aminobenzoic acid (III), obtained on hydrolysis of (II), was crystallised from boiling water in shining flat needles, m.p. 213° (decomp.) (Kunckell and Richartz, *loc. cit.*). (Found: Equiv., 168.0; N, 8.2; Cl, 20.5. Calc. for $C_7H_6O_2NCl$: Equiv., 171.5; N, 8.2; Cl, 20.7%).

(III) on diazotisation and subsequent treatment with cuprous chloride solution afforded 2:4-dichlorobenzoic acid. It was crystallised from boiling water, m.p. 161° (mixed m.p. with an authentic sample, undepressed).

Friedel-Crafts' Acylation of o-Chloroacetanilide with Chloroacetyl Chloride

ω-4-Dichloro-3-acetaminoacetophenone (IV).—The condensation of *o*-chloroacetanilide (10 g.) with chloroacetyl chloride (10 g.) in presence of finely powdered anhydrous aluminium chloride (30 g.) was carried out by following the procedure described previously. The compound (IV) obtained was crystallised from boiling dilute alcohol as a white powder, m.p. 126°, yield 8 g. (Found: N, 5.6; Cl, 28.4. $C_{10}H_9O_2NCl_2$ requires N, 5.7; Cl, 28.9%).

ω-4-Dichloro-3-aminoacetophenone, obtained on hydrolysis of (IV) as a yellow powder, was crystallised from dilute alcohol in small yellowish needles, m.p. 92-94°. (Found: N, 6.5; Cl, 34.2. $C_8H_7ONCl_2$ requires N, 6.9; Cl, 34.8%).

N-Benzoyl derivative of the above amino base was crystallised from alcohol as a pinkish crystalline powder, m.p. 120-22°. (Found: N, 4.7; Cl, 22.6. $C_{15}H_{11}O_2NCl_2$ requires N, 4.5; Cl, 23.2%).

3-Acetamino-4-chlorobenzoic acid (V) was obtained on oxidation of (IV) with a neutral permanganate solution. It was crystallised from boiling water in white needles, m.p. 263-64°. (Found: Equiv., 216.0; N, 6.7; Cl, 16.4. Calc. for $C_9H_8O_3NCl$: Equiv., 213.5; N, 6.6; Cl, 16.6%).

3-Amino-4-chlorobenzoic acid (V-B), obtained on hydrolysis of (V) with hot 5% HCl, was crystallised from boiling water in flat needles, m.p. 212-15°. (Found: Equiv., 169.0; N, 8.0; Cl, 20.4. Calc. for $C_7H_6O_2NCl$: Equiv., 171.5: N, 8.2; Cl, 20.7%)

(V-B) was also obtained by an alternate method, recorded below, for the purpose of comparison.

A continuously stirred mixture of 3-nitro-4-chlorobenzoic acid (1.5 g.) (Hübner, *Z. Chem.*, 1866, 615), water (25 c.c.), acidulated with a few drops of acetic acid, and iron powder (3 g.) was heated on a steam-bath for half an hour. The solution was then made alkaline with caustic soda solution, boiled and filtered. The cooled filtrate was just acidified with acetic acid and extracted with ether. (V-B), obtained on evaporation of the ether, was crystallised from boiling water, m.p. 212-15° (Hübner and Biedermann, *Annalen*, 1868, **147**, 258); its m.p. on admixture with the same obtained by the above method remained undepressed; its *N*-acetyl derivative (V) melted at 263-64° (Bamberger, *loc. cit.*); mixed m.p. with (V), obtained as above, remained undepressed.

4-Acetamino-3-chlorobenzoic acid (VI) was synthesised by oxidising 3-chloro-4-acetaminotoluene (VII) with a neutral permanganate solution, the latter being obtained on chlorination of aceto-*p*-toluidide (Reverdin and Crepieux, *loc. cit.*). It was crystallised from boiling water in small needles, m.p. 230-31°. (Found: Equiv., 217.3; N, 6.7; Cl, 16.7. $C_9H_8O_3NCl$ requires equiv., 213.5; N, 6.6; Cl, 16.6%). The mixed m.p. of this acid with (V) was depressed (210-17°).

Friedel-Crafts' acylation of *o*-chloroacetanilide with acetyl chloride failed while that of *p*-chloroacetanilide with all these acid halides including chloroacetyl chloride failed.

Friedel-Crafts' Acylation of 2-Acetamino-4-chlorotoluene with Chloroacetyl Chloride

ω-2 Dichloro-5-methyl-4-acetaminoacetophenone (VIII) was obtained on condensation of 2-acetamino-4-chlorotoluene (10 g.) with chloroacetyl chloride (10 g.) in presence of finely powdered anhydrous aluminium chloride (30 g.), following the procedure described above. It was crystallised from alcohol in thin shining yellowish plates, m.p. 168-70°, yield 9 g. (Found: N, 5.1; Cl, 26.8 $C_{11}H_{11}O_2NCl_2$ requires N, 5.4; Cl, 27.3%).

4-Amino-5-methyl-ω-2-dichloroacetophenone, obtained on hydrolysis of (VIII), was crystallised from acetone-petrol ether mixture as clusters of long thin, brownish needles, m.p. 122-23°. (Found: N, 6.2; Cl, 32.2. $C_9H_9ONCl_2$ requires N, 6.4; Cl, 32.6%).

This base did not furnish a coloured product similar to an indigo dye on fusion with potassium hydroxide, a characteristic test for an *o*-amino-ω-chloroacetophenone.

N-Benzoyl derivative of 4-amino-5-methyl-ω-2-dichloroacetophenone was crystallised from alcohol as a yellow powder, m.p. 200°. (Found: N, 4.5; Cl, 21.6. $C_{16}H_{13}O_2NCl_2$ requires N, 4.35; Cl, 22.0%).

4-Acetamino-5-methyl-2-chlorobenzoic Acid (IX).—(VIII) on oxidation with neutral permanganate solution afforded (IX), which was crystallised from boiling water as white granules, m.p. 306-308° (decomp.). (Found: Equiv., 231.2; N, 6.0; Cl, 15.3. $C_{10}H_{10}O_3NCl$ requires equiv., 227.5; N, 6.15; Cl, 15.6%).

Ullmann's Condensation of 4-Acetamino-5-methyl-2-chlorobenzoic Acid with Aniline

4-Methyl-5-acetaminodiphenylamine-2-carboxylic Acid.—A mixture of 4-acetamino-5-methyl-2-chlorobenzoic acid (0.5 g.), fused potassium carbonate (0.5 g.), aniline (5 c.c.) and a trace of copper powder was refluxed in an oil-bath at about 190° for about 2 hours. After removing excess of aniline by steam distillation, the reaction mixture was filtered hot, concentrated and acidified, when the corresponding diphenylamine-2-carboxylic acid derivative separated out. It was crystallised from alcohol as small granules, m.p. 214-16° (decomp.). (Found: Equiv., 279.7; N, 9.6. $C_{16}H_{16}O_3N_2$ requires equiv., 284.0; N, 9.85%).

M. R. Science Institute,
Gujarat College,
Ahmedabad.

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PHYSICO-CHEMICAL STUDIES ON THE COMPOSITION OF COMPLEX THIOSULPHATES OF METALS. PART I. COMPOSITION OF CADMIUM THIOSULPHATE BY CONDUCTOMETRIC AND THERMOMETRIC TITRATIONS AND BY JOB'S METHOD OF CONTINUED VARIATION

By M. S. Bhadraver and J. N. Gaur

The composition of cadmium thiosulphate has been studied by conductometric and thermometric titrations between sodium thiosulphate and cadmium chloride solutions, employing different concentrations of the reactants in aqueous and aqueous alcoholic medium both by direct and reverse methods. The composition arrived at by both direct and reverse methods is CdS_2O_3 in the ratio of 1:1 ($Cd : S_2O_3$).

As the reference in literature about the study of cadmium thiosulphate is meagre and variable formulae are given, e.g., $CdS_2O_3.2H_2O$, $Na_2S_2O_3.2CdS_2O_3.7H_2O$, $Na_2S_2O_3.3CdS_2O_3.9H_2O$, $Na_2S_2O_3.CdS_2O_3.3H_2O$ (vide Mellor, "Comprehensive Treatise of Inorganic Chemistry", Vol. XI, p. 546), this investigation has been undertaken. The method of Job's continued variation (*Compt. rend.*, 1925, **180**, 928) has been further applied and it has been varified that the reaction between cadmium chloride and sodium thiosulphate takes place in the ratio of 1 : 1. Besides, the value of degree of dissociation for any particular concentration ($c = 0.025$) has been determined to be 3.000×10^3.

Experimental

Merck's reagents were used. Sodium thiosulphate was standardised against standard KIO_3 solution. Cadmium was estimated as cadmium molybdate (Vogel, "Text Book of Quantitative Inorganic Analysis", p. 428).

With different concentrations of the two salts in solution, conductometric and thermometric titrations were carried out by direct and reverse methods. The titrations were also carried out both in aqueous and aqueous alcoholic medium, the maximum alcoholic concentration in the latter case being 20% by volume. For the study by Job's method, conductometric measurements, both in equimolecular and non-equimolecular solutions, were made. Summary observations of conductometric and thermometric titrations are shown in Tables I and II.

FIG. 4

FIG. 2

Reverse titrations

Direct titrations

FIG. 3

FIG. 1

TABLE I

Conductometric titrations.

Curve No.	Fig. No.	$CdCl_2$.	$Na_2S_2O_3$.	Medium.	Points showing breaks. Calc.	Obs.	Formula supported.	
				Direct titrations.				
I	1	M/5	M/20 20 c.c.	Aq.	5.0	5.5	CdS_2O_3	(1:1)
II	1	,,	18	Alc. 10%	4.5	5.0	,,	,,
III	1	,,	16	,, 20	4.0	4.5	,,	,,
I	2	M/40	M/400 20 c.c.	Aq.	2.0	2.2	,,	,,
II	2	,,	18	Alc. 10%	1.8	1.9	,,	,,
III	2	,,	16	,, 20%	1.6	1.7	,,	,,
				Reverse titrations:				
I	3	M/40 20 c.c.	M/5	Aq.	2.45	2.4	,,	,,
II	3	18	,,	Alc. 10%	2.24	2.2	,,	,,
III	3	16	,,	,, 20%	2.00	2.0	,,	,,
I	4	M/400 20 c.c.	M/40	Aq.	2.0	2.0	,,	,,
II	4	18	,,	Alc. 10%	1.8	1.85	,,	,,
III	4	16	,,	,, 20%	1.6	1.60	,,	,,

TABLE II

Thermometric titrations.

Fig. No.	Curve No.	$CdCl_2$.	$Na_2S_2O_3$.	Medium.	Points showing breaks. Calc.	Obs.	Formula supported.	
				Direct titrations.				
1	I	M/8	M/100 20 c.c.	Aq.	3.6	3.6	CdS_2O_3	(1:1)
1	II	,,	18	Alc. 10%	2.44	2.44	,,	,,
1	III	,,	16	,, 20	1.28	1.20	,,	,,
1	IV	M/8	M/40	Aq.	4.00	4.20	,,	,,
1	V	,,	18 c.c.	Alc. 20	3.60	3.60	,,	,,
1	VI	,,	16	,, 20	3.20	3.20	,,	,,
				Reverse titrations.				
2	I	M/40 20 c.c.	M/5	Aq.	2.5	2.40	,,	,,
2	II	18 ,,	,,	Alc. 10%	2.25	2.25	,,	,,
2	III	16 ,,	,,	,, 20	2.00	2.00	,,	,,
2	IV	M/100 20 c.c.	M/5	Aq.	1.00	1.00	,,	,,
2	V	18 ,,	,,	Alc. 10	0.90	0.90	,,	,,
2	VI	16 ,,	,,	,, 20	0.80	0.70	,,	

TABLE III

Job's method.

$M/35$-$CdCl_2.5/2H_2O$ solution (35 c.c.) in cell. Molar sodium thiosulphate solution added from burette. Initial value of conductance $= 11.75 \times 10^{-3}$. Temp. $= 39°$ (Fig. 5, Curve II).

Thio added.	Increase in condy. over initial value after each dilution.	Thio added.	Increase in condy. over initial value after each dilution	Thio added.	Increase in condy. over initial value after each dilution.	Thio added.	Increase in condy. over initial value after each dilution.
0.0 c.c.	0.0×10^{-3}	2.4	8.25×10^{-3}	0.2 c.c.	0.75×10^{-3}	2.6	9.25×10^{-3}
0.4	1.00	2.8	9.75	0.6	1.50	3.0	10.25
0.8	2.50	3.2	11.25	1.0	3.50	3.4	11.75
1.2	4.25	3.6	12.25	1.4	4.75	3.8	13.25
1.6	5.75	4.0	13.75	1.8	6.25	4.2	14.25
2.0	6.75			2.2	7.75		

TABLE IV

Titration of $M/50$-$CdCl_2$ with $M/400$-thio. Temp. $= 36°$.

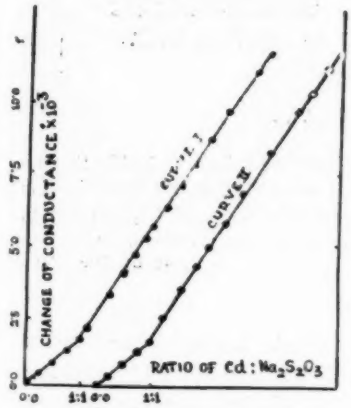
$CdCl_2$.	$I/R \times 10$ of soln. in col. 1 (each diluted to 35 c.c. $= C_1$).	$Na_2S_2O_3$ added.	$I/R \times 10$ of soln. in col. 3 (each diluted to 35 c.c $= C_2$).	$C_1 + C_2 = C_3$.	$I/R \times 10$ of mix. of solns. in columns 1 and $3 = C_4$.	$C_3 - C_4$.
35.0 c.c.	25.0×10^{-3}	0.0 c.c.	0.0×10^{-3}	0.0	25.0×10^{-3}	0.0×10^{-3}
23.0	22.8	12.0	0.99	20.09	23.0	0.0
22.5	20.0	12.5	0.76	20.76	20.02	0.74
22.0	20.0	13.0	0.86	20.86	20.10	0.76
21.0	19.5	14.0	0 83	20.33	19.53	0.80
19.0	18.0	16.0	0.96	18.96	18.05	0.91
17.0	16.7	18.0	1.05	17.75	16.87	0.88
15.0	15.2	20.0	1.13	16.15	15.15	1.00
13.0	13.5	22.0	1.20	14.70	13.63	0.97
12.0	13.0	23.0	1.35	14.35	13.39	0.96
0.0	...	35.0	1.65	1.65	1.65	0.00

DISCUSSION

It is evident from Tables I and II that both the methods by direct and reverse titrations suggest the formation of only one compound, CdS_2O_3, in the ratio of 1 : 1 ($Cd : S_2O_3$).

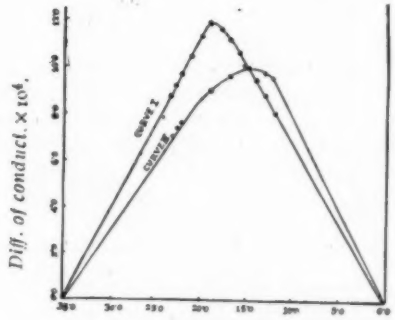
It is observed from Fig. 5, Curve II that a sharp break occurs in the ratio as 1 : 1($Cd : S_2O_3$), as supported by conductometric and thermometric titrations. Hence, it can be concluded that the reaction between cadmium chloride and sodium thiosulphate occurs in the ratio 1 : 1 (vide Table III) of equimolecular solutions of cadmium chloride where the maximum is obtained in each case in that proportion when the divergence from the additivity rule is plotted against the decomposition of the mixture (Fig. 6, Curves I and II).

FIG. 5
Job's method.



I: 35 c.c of $M/40$-$CdCl_2$+M-thio.
II: „ $M/35$ „ „

FIG. 6
Job's method.



$CdCl_2$ *added in c c.*
I: $M/40$-$CdCl_2$+$M/400$- thio.
II: $M/10$ „ $M/40$- „

The degree of dissociation of cadmium thiosulphate at a particular dilution has been calculated from the formula

$$K = \frac{\{c(pc-1)\,x-1\}^2}{\{(pc-1)\,(1-2x)\}}$$

where c is the molar concentration of cadmium chloride, pc is the molar concentration of sodium thiosulphate solution reacting with $(1-x)$ c.c. of cadmium chloride to give maximum effect.

Table III	Fig.	Curve No.	c.	pc.	x.	$K \times 10^3$.
	6	II	0.01	4.0	0.52	3.00

Thus, the dissociation constant at $c = 0.01$ is calculated to be 3.00×10^{-3}.

Potentiometric studies on the problem are in progress and will be communicated shortly in future.

CHEMISTRY DEPARTMENT,
LOHIA COLLEGE,
CHURU, RAJASTHAN.

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PHYSICO-CHEMICAL STUDIES ON THE COMPOSITION OF COMPLEX THIOSULPHATES OF METALS. PART II. THERMOMETRIC INVESTIGATIONS OF THE COMPOSITION OF SILVER THIOSULPHATE COMPLEXES

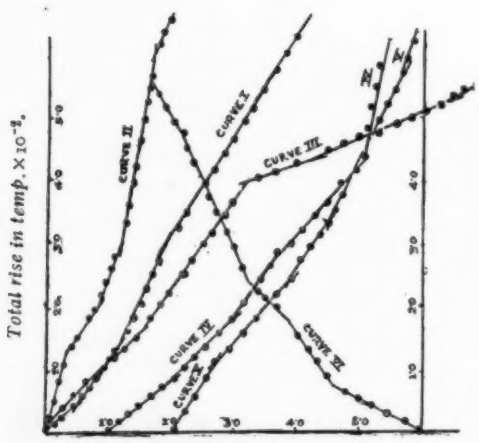
By J. N. Gaur and M. S. Bhadraver

The formation and composition of silver thiosulphate complexes have been studied by thermometric measurements at several concentrations, both by direct and reverse methods. The direct titration curves yield four distinct breaks corresponding to the formation of $Na_3Ag(S_2O_3)_2$, $NaAgS_2O_3$, $Na_5Ag_3(S_2O_3)_4$ and $Ag_2S_2O_3$ whereas in the reverse titrations only two breaks are observed, suggesting the formation of $NaAgS_2O_3$ and $Ag_2S_2O_3$. The results support the conclusions arrived at by the conductometric studies on the same complexes by Saxena and Jain.

E. Merck's (guaranteed extra pure) reagents were used. Silver nitrate solution was standardised against a known solution of NaCl (Vogel, "Text Book of Quantitative Inorganic Analysis", 1951, p. 251). Sodium thiosulphate solution was prepared by weighing and was checked iodometrically against a standard solution of KIO_3 as in Part I (this *issue*, p. 103). Using different concentrations of the reactants, the titrations were performed by direct and reverse methods. The experimental arrangement used was the same as has been described by Haldar (this *Journal*, 1946, **23**, 147). The titrations were also carried out in the presence of alcohol up to a total concentration of 20% by volume. The total rise in temperature was then plotted against the titre in c.c. A correction was applied by carrying out 'blank' experiments using water as titre instead of silver nitrate and sodium thiosulphate to account for dilution effect.

FIG. 1

Direct titrations.

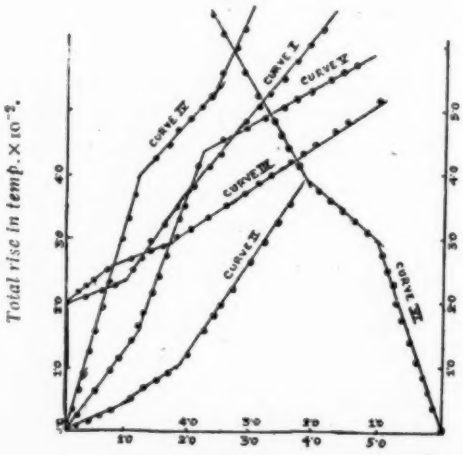


$AgNO_3$ *added in c.c.*

I-III: *M*/5-$AgNO_3$ + *M*/100- thio.
IV-VI: *M*/10- „ „ „

FIG. 2

Reverse titrations.



Thio added in c.c.

I-III: *M*/10- thio + *M*/200- $AgNO_3$.
IV-VI: *M*/5- „ *M*/40- „

TABLE I

Summary of observations of thermometric titrations.

Fig. No.	Curve No.	$AgNO_3$.	$Na_2S_2O_2$.	Medium.	Points showing breaks Calc.	Obs.	Ratio.
	Direct titrations :						
1	I	*M*/5	*M*/100	Aq.	0.50	0.50	1 :2
,,	,,	,,	20 c c.	,,	0.33	0.33	3 :4
				,,	1.00	1.00	1 :1
,,	,,	,,	,,	,,	2.00	2.00	2 :1
,,	II	,,	18 c.c.	Alc. 10%	0.45	0.40	1 :2
,,	,,	,,	,,	,,	0.90	0.90	1 :1
,,	,,	,,	,,	,,	1 20	1.20	3 :4
,,	,,	,,	,,	,,	1.80	1.80	2 :1
,,	III	,,	,,	Alc. 20%	0.80	0.80	1 :2
,,	III	,,	16	,,	1.60	1.60	1 :1
,,	,,	,,	,,	,,	2.13	2.00	3 :4
,,	,,	,,	,,	,,	3.20	3.20	2 :1
2	IV	*M*/10	*M*/100	Aq.	1.00	1.0	1 :2
,,	,,	,,	,,	,,	2.00	2.6	1 :1
,,	,,	,,	,,	,,	2.66	2.6	3 :4
,,	,,	,,	,,	,,	4.00	4.0	2 :1
1	V	,,	,,	Alc. 10%	0.96	0.9	1 :2
,,	,,	,,	,,	,,	1.80	1.8	1 :1
,,	,,	,,	,,	,,	2.40	2.4	3 :4
,,	,,	,,	,,	,,	3 60	3.6	2 :1
1	VI	,,	,,	Alc. 20%	0.80	0.8	1 :2
,,	,,	,,	,,	,,	1.60	1.6	1 :1
,,	,,	,,	,,	,,	2.13	2.1	3 :4
,,	,,	,,	,,	,,	3.20	3.2	2 :1
	Reverse titrations :						
,,	I	*M*/200	*M*/10	Aq.	0.50	0.45	1 :2
,,	,,	,,	,,	20 c.c.	1.00	1 00	1 :1
,,	II	18 c.c.	,,	Alc. 10%			
				,,	0.45	0.42	1 :2
,,	III	,,	,,	,,	0.90	0.90	1 :1
,,	,,	16 c c.	,,	Alc. 20%	0.40	0.35	1 :2
,,	,,	,,	,,	,,	0.80	0.80	1 :1
2	IV	*M*/40	*M*/5	Aq.	1.25	1.26	1 :2
,,	,,	,,	,,	,,	2.50	2.50	1 :2
,,	V	18 c.c.	,,	Alc. 10%	1.12	1.10	1 :2
				,,	2.25	2.20	1 :1
,,	VI	16	,,	Alc 20%	1.00	1.00	1 :2
				,,	2.00	2.00	1 :1

From Table I it is evident that in case of direct titrations (Fig. 1) there are four distinct breaks when the molecular ratios of the reactants are : 1 : 2, 1 : 1, 3 : 4 and 2 : 1 corresponding to the formation of $Na_3Ag(S_2O_3)_2$, $NaAg(S_2O_3)$, $Na_5Ag_3(S_2O_3)_4$ and

$Ag_2S_2O_3$ respectively, whereas in the reverse titrations (Fig. 2) only two breaks are obtained in support of the formation of the compounds $Ag_2S_2O_3$ and $NaAg(S_2O_3)$.

Basset and Lemon (Fritz Ephraim, "Text Book of Inorganic Chemistry", 1954, p. 584) have identified the following compounds from a phase rule study: $NaAg(S_2O_3).H_2O$, $Na_3Ag(S_2O_3)_2.2H_2O$, $Na_5Ag_3(S_2O_3)_4\ 4H_2O$ and $NaAg(S_2O_3)_2.H_2O$. While the formation of the first three compounds has been confirmed by our thermometric titrations, there is no evidence for the formation of the compounds $NaAg(S_2O_3)$ and $Ag_2S_2O_3$.

In the light of the thermometric results, the formation of the compounds $Ag_2S_2O_3.4Na_2S_2O_3$, as obtained by Dey and Musrani (*Proc. Nat. Acad. Sci.*, 1947, **16A**, 37) by analysis is also untenable.

Our thermometric results are in accordance with conductometric results of Saxena and Jain (this *Journal*, 1954, **31**, 319) showing the formation of $Na_3Ag(S_2O_3)_2$, $NaAgS_2O_3$, $Na_5Ag_3(S_2O_3)_4$ and $Ag_2S_2O_3$ in direct titrations and $Ag_2S_2O_3$ and $NaAgS_2O_3$ in reverse titrations as in this thermometric investigation.

The potentiometric studies are in progress for these complexes and will be communicated shortly.

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LOHIA COLLEGE, CHURU,
RAJASTHAN.

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FRIES MIGRATION OF ESTERS OF 2:4-DIBROMOPHENOL

By C. M. Christian and G. C. Amin*

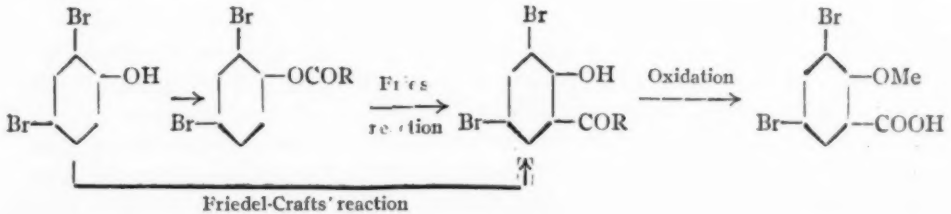
The Fries migration of 2:4-dibromophenyl acetate, propionate and butyrate affords 3:5-dibromo-2-hydroxy-acetophenone, -propiophenone and -butyrophenone respectively. The Friedel-Crafts acylation of 2:4-dibromophenol also affords the same products. The benzoate, however, yields a product which is not a ketone. Thus, the two bromine atoms in the nucleus do not retard the Fries reaction.

The Fries migration of various halogen-substituted phenolic esters has been studied by several workers (Klarmann *et al.*, *J. Amer. Chem. Soc.*, 1933, **55**, 2576, 4657; Chakravarti and Majumdar, this *Journal*, 1939, **16**, 151; Sen and Parmar, *ibid.*, 1953, **30**, 59; Tiwari and Tripathi, *ibid.*, 1954, **31**, 841, 1956, **33**, 211; Kindler and Oelschlanger, *Ber*, 1954, **87**, 194; Chen and Chang, *J. Chem. Soc.*, 1958, 146). In the present communication, the Fries isomerisation of the esters of 2:4-dibromophenol has been described.

2:4-Dibromophenyl acetate (II: R = Me) on migration yields a product which has been assigned the constitution 2:4-dibromo-6-acetylphenol (III: R = Me) as its methoxy derivative affords 3:5-dibromo 2-methoxybenzoic acid on oxidation. Its various reactions (Joshi and Shah, this *Journal*, 1954, **31**, 221) and its similarity with the migration of 2:4-dichlorophenyl acetate (Chien and Yin, *J. Chinese Chem. Soc.*, 1939, **7**, 40) also point to the same structure. It was also synthesised by brominating *o*-hydroxyacetophenone, the mixed melting point with the migrated product remaining undepressed.

Similarly, 2:4-dibromophenyl propionate (II: R = Et) and butyrate (II, R= *n*-Pr) on Fries migration gave 2:4-dibromo-6-propionyl- (III: R= Et) and -6-butyryl- (III, R= *n*-Pr) phenols respectively. 2:4-Dibromophenyl benzoate (II: R= Ph) did not rearrange to the expected 2:4-dibromo-6-benzoylphenol, but gave a product, the constitution of which had not been determined.

The Friedel-Crafts acetylation, propionylation and butyrylation afforded 2:4-dibromo-6-acylphenols, the mixed melting points of which corresponded to those obtained by the Fries reaction.



(I) (II) (III) (IV)

[R= Me, Et, *n*-Pr, Ph]

* Present address : Chemistry Dept., M. N. College, Visnagar (N.G.).

EXPERIMENTAL

2 : 4-Dibromophenyl acetate (II : R= Me) was prepared by heating 2 :4-dibromophenol (I, 10 g.) (Hewitt *et al.*, *J. Chem. Soc.*, 1904, **85**, 1227) with acetic anhydride (4.4 g.) and a few drops of H_2SO_4 on a water-bath for 3 hours. The oil obtained after the usual treatment was collected at 275° as a yellow liquid. It solidified on keeping, m.p. 36°.

Fries Migration of 2 :4-Dibromophenyl Acetate : 3 :5-Dibromo-2-hydroxyacetophenone (III : R= Me).—2 : 4-Dibromophenyl acetate (II : R= Me ; 3 g., 1 *M*) was thoroughly mixed with aluminium chloride (4.4 g., 3.3 *M*) and the mixture was heated in an oil-bath at 150° for 2 hours. After the reaction was over, the mixture was treated with ice and HCl. A greenish yellow solid that separated was collected, washed with cold water and crystallised from alcohol in long yellowish white needles, m.p. 110°, yield 1.4 g. It is soluble in sodium hydroxide with a yellow colour and develops a dark brown colour with alcoholic ferric chloride. It is soluble in alcohol, benzene and acetic acid. (Found : Br, 54.20. $C_8H_6O_2Br_2$ requires Br, 54.42%). The above reaction at 100° and 120° also gave similar results.

The *oxime* of the above ketone, prepared as usual, was crystallised from alcohol in white shining silky needles, m.p. 203° (decomp.). (Found : Br, 51.50. $C_8H_7O_2NBr_2$ requires Br, 51.[illegible]).

The *semicarbazone* was crystallised from alcohol as a yellowish white granular solid, m.p. 280° (decomp.). (Found : Br, 45.33. $C_9H_9O_2N_3Br_2$ requires Br, 45.57%).

The *acetate*, prepared by acetic anhydride-pyridine method, was crystallised from alcohol in small white needles, m.p. 89°. (Found : Br, 47.42. $C_{10}H_8O_3Br_2$ requires Br, 47.61%).

The *methoxy* derivative, prepared by dimethyl sulphate-acetone-potassium carbonate method, was crystallised from alcohol in light brown needles, m.p. 55°. (Found : Br, 51.67. $C_9H_8O_2Br_2$ requires Br, 51.90%).

Formation of 3 :5-Dibromo-2-methoxybenzoic Acid (IV) *from 3 :5-Dibromo-2-methoxyacetophenone.*—The methoxy compound (1 g.), suspended in 5% alkali (100 c.c.), was oxidised by heating with $KMnO_4$ (4 g.) for 8 to 10 hours. After the reaction was over, the solution was filtered off and acidified. The solid that separated on cooling was recrystallised from water in colorless shining plates, m.p. and the mixed m.p. with an authentic sample being 195° (Fries and Moskopp, *Annalen*, 1911, **372**, 204).

Friedel-Crafts' Acetylation of 2 : 4-Dibromophenol.—To a solution of anhydrous aluminium chloride (17.5 g., 3.3*M*) in dry nitrobenzene (60 c.c.) were added 2 :4-dibromophenol (10 g., 1 *M*) and acetic anhydride (4.45 g., 1.1 *M*). The reaction mixture was kept at room temperature overnight and was then heated on an oil-bath at 120° for 2 hours. After the usual treatment with ice and HCl, the nitrobenzene was removed by steam-distillation and the residual contents were cooled and filtered. The yellowish product obtained was crystallised from alcohol in yellowish white long needles, m.p. 110°, yield 4.8 g. It was found to be 3 :5-dibromo-2-hydroxyacetophenone by direct comparison with the Fries rearrangement product.

Fries Migration of 2:4 Dibromophenyl Propionate : Formation of 3:5-Dibromo-2-hydroxypropiophenone (III : R = Et).—The Fries rearrangement of 2:4-dibromophenyl propionate (II : R = Et, 3 g., 1*M*) (b.p. 275-80°) by anhydrous aluminium chloride (4.3 g., 3.3 *M*) at 150° for 2 hours gave a greenish yellow solid after the usual treatment. It was crystallised from alcohol in yellowish needles, m.p. 121°, yield 1.0 g. (Found : Br, 51.71. $C_9H_8O_2Br_2$ requires Br, 51.94%).

The *oxime*, prepared as before, was crystallised from alcohol in white needles, m.p. 180° (decomp.). (Found : Br, 49.20. $C_9H_9O_2NBr_2$ requires Br, 49.52%).

The *semicarbazone*, prepared as usual, was crystallised from alcohol in yellowish white needles, m. p. 180° (decomp.). (Found : Br, 43.55. $C_{10}H_{11}O_2N_3Br_2$ requires Br, 43.82%).

The *methoxy* derivative, prepared as before, was crystallised from alcohol in white needles, m.p. 54°. (Found : Br, 49.45. $C_{10}H_{10}O_2Br_2$ requires Br, 49.68%). The *oxidation* of methoxy derivative gave 3:5-dibromo-2-methoxybenzoic acid (IV), identified by the mixed melting point.

The Friedel-Crafts propionylation of 2:4-dibromophenol afforded 3:5-dibromo-2-hydroxypropiophenone, identified by the mixed melting point.

Fries Migration of 2:4-Dibromophenyl Butyrate : Formation of 3:5-Dibromo-2-hydroxybutyrophenone (III : R = *n*-Pr).—A mixture of 2:4-dibromophenyl butyrate (II : R = *n*-Pr ; 3 g., 1*M*) (b.p. 295-300°) and anhydrous aluminium chloride (4.1 g., 3.3*M*) was heated in an oil-bath at 150° for 2 hours. The oily liquid obtained after decomposition was extracted with ether, dried over fused sodium sulphate and vacuum-distilled. The fraction was collected at 155-60°/3.5 mm, yield 1.3 g. (Found : Br, 49.49. $C_{10}H_{10}O_2Br_2$ requires Br, 49.68%).

The *oxime* was crystallised from alcohol in white plates, m.p. 178° (decomp.). (Found : Br, 47.14. $C_{10}H_{11}O_2NBr_2$ requires Br, 47.46%).

The *semicarbazone*, as white granules from alcohol, remained unmelted till 280°. (Found : Br, 41.95. $C_{11}H_{13}O_2N_3Br_2$ requires Br, 42.21%).

The *benzoate* melted at 56-58° after crystallising from alcohol. (Found : Br, 37.26. $C_{17}H_{14}O_3Br_2$ requires Br, 37.54%). The *oxidation* of the methoxy compound produced the same acid (IV), identified by mixed m p.

The Friedel-Crafts butyrylation of 2:4-dibromophenol gave 3:5-dibromo-2-hydroxybutyrophenone which was confirmed by preparing the oxime having the same mixed m.p. with that described above.

Attempted Fries Migration of 2:4-Dibromophenyl Benzoate.—The reaction mixture of 2:4-dibromophenyl benzoate (II : R = Ph ; 3 g., 1*M*) (m.p. 96°) and anhydrous aluminium chloride (3.7 g., 3.3 *M*) was heated at 120° for 2 hours. A yellow solid that separated after decomposition of the reaction mixture was crystallised from benzene-petrol mixture in white needles, m.p. 183°. (Found : Br, 53.73. $C_{19}H_{12}O_2Br_4$ requires Br, 54.06%).

It is insoluble in dilute alkali and does not respond to alcoholic ferric chloride test. The reaction was studied under a variety of conditions with and without nitrobenzene, but the expected ketone (m.p. 129°) could not be isolated in any case. The Friedel-Crafts benzoylation of 2 : 4-dibromophenol also produced the same compound.

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M. R. Science Institute,
Gujarat College, Ahmedabad 6.

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SYNTHESIS OF ANTIMALARIALS. HALOGENATED ACRIDINES

By A. G. Munshi and K. S. Nargund

Several methoxy derivatives of dihalogenated 5-substituted aminoacridines have been prepared and their properties studied and described.

A large amount of work has been done to prepare suitable acridine derivatives as antimalarial drugs (Wiselogle, "Survey of Antimalarial Drugs", 1941-45, Vol. II, Part II). Magidson and Grigorovsky (*Ber.*, 1936, **69**, 396) observed that 5-amino derivatives containing chlorine atom in any position exhibited antimalarial property. Moreover, Whitmore *et al.* observed that the introduction of chlorine atoms in demethoxy-atabrine afforded a product, 2: 8-dichloro-5-(4-diethylamino-1-methylbutyl)-aminoacridine, of high antimalarial activity (*J. Amer. Chem. Soc.*, 1946, **68**, 1596).

Several compounds with two chlorine atoms in the nucleus, other than the one containing methoxy group, were synthesised by the present authors (this *Journal*, 1957, **34**, 367). It has therefore been considered worthwhile to synthesise compounds with two chlorine atoms in the same nucleus which contains a methoxy group.

3 : 5-Dichloro-4-methoxyaniline, required in the synthesis of such a derivative, viz., 3′ : 5′-dichloro-4′-methoxydiphenylamine-2-carboxylic acid, has been prepared for the first time.

p-Nitrophenol, dissolved in concentrated hydrochloric acid, on chlorination by potassium chlorate afforded 3 : 5-dichloro-4-hydroxynitrobenzene. Methylation of this compound could not be effected by usual methods. After several trials, it was observed that the silver salt of 2 : 6-dichloronitrophenol, when treated with an excess of methyl iodide in alcoholic solution, yielded the expected 2 : 6-dichloro-4-methoxynitrophenol. This nitro derivative was reduced with tin and hydrochloric acid, when 2 : 6-dichloro-4-methoxyaniline was obtained. This substituted aniline on condensation with *o*-chlorobenzoic acid (Ullmann's condensation) furnished 3′ : 5′-dichloro-4′-methoxydiphenylamine-2-carboxylic acid.

Phosphorus oxychloride method, when used to prepare 5-chloroacridine from 3′ : 5′-dichloro-4′-methoxydiphenylamine-2-carboxylic acid, yielded only a small amount of 5-chloroacridine, most of the acid having been converted into acridone. Where 5-chloroacridine formation was not possible or a mixture of both acridine and acridone was obtained, a modified method had to be employed in which the acid chloride was first converted into its amide by heating it with an appropriate amine and subsequent cyclisation of the amide by heating with phosphorus oxychloride.

Experimental

3 : 5-*Dichloro-4-hydroxynitrobenzene* was obtained by adding potassium chlorate solution (3.6 g. in 75 c.c. water) to the cooled solution of *p*-nitrophenol (6.4 g.) in HCl (conc., 250 c.c.). It was filtered, washed with water and crystallised from benzene in small white needles, m.p. 125° (decomp.) (Found : Cl, 34.15. $C_6H_3O_3NCl_2$ requires Cl, 34.13%).

3 : 5-*Dichloro*-4-*methoxynitrobenzene* was prepared by keeping the mixture of silver salt of 3 : 5-dichloro-4-hydroxynitrobenzene (5 g.), suspended in absolute alcohol (30 c.c.), and methyl iodide (10 g.) at room temperature overnight. It was then refluxed for 5 hours on a water-bath and filtered hot. It was crystallised from alcohol in white needles, m.p. 102°. (Found : Cl, 32.08. $C_7H_5O_3NCl_2$ requires Cl, 31.98%).

3 : 5-*Dichloro*-4 *methoxyaniline* was obtained by heating a mixture of 3 : 5-dichloro-4-methoxynitrobenzene (8 g.), HCl (conc., 40 c.c.) and tin (16 g.). The reduced product was crystallised from alcohol in white long needles, m.p. 87°. (Found : Cl, 37.4. $C_7H_7ONCl_2$ requires Cl, 36.97%).

3′ : 5′-*Dichloro*-4′-*methoxydiphenylamine*-2-*carboxylic acid* was obtained by refluxing a mixture of the preceding amine (4 g.), *o*-chlorobenzoic acid (3 g.), anhydrous potassium carbonate (3 g.), amyl alcohol (30 c.c.) and copper powder (0.2 g.) at 155° for 5 hours. After washing with boiling water to remove unchanged *o*-chlorobenzoic acid, it was crystallised from acetic acid in small white needles, m.p. 213°. (Found : Cl, 28.85 ; equiv., 312.3. $C_{14}H_{11}O_3NCl_2$ requires Cl, 28.76% ; equiv., 312).

3′ : 5′-*Dichloro* 4′-*methoxydiphenylamine*-2-*carboxylic acid chloride* was obtained by heating the acid (1 g.) with thionyl chloride (5 c.c.) in presence of benzene (20 c.c.). It separated on long-standing as yellowish green plates, m.p. 195°. (Found : Cl, 32.99. $C_{14}H_{10}O_2NCl_3$ requires Cl, 32.23%).

2 : 4 : 5-*Trichloro*-3-*methoxyacridine* was obtained by refluxing the mixture of the above amine -2-carboxylic acid (1 g.) and $POCl_3$ (6 g.) at 120° for 3 hours. On decomposition by ice-cold ammonia, a mixture of acridine and acridone was obtained. On treatment of the mixture with toluene, 5-chloroacridine separated from acridone which was found to be insoluble. 5-Chloroacridine was crystallised from toluene in greenish yellow needles, m.p. 159°. (Found : Cl, 34.11. $C_{14}H_8ONCl_3$ requires Cl, 34.08%).

3-*Methoxy*-2 : 4-*dichloro*-5-(γ-*morpholinopropyl*)-*aminoacridine dihydrochloride* was prepared by heating a mixture of 2 : 4 : 5-trichloro-4-methoxyacridine (1 g.), γ-morpholinopropylamine (0.5 g.) and freshly distilled phenol (5 g.) at 100° for 3 hours. Into the alcoholic extract of the reaction mixture dry HCl gas was passed. On addition of ether, a yellow solid separated which was crystallised from alcohol, m.p. 208° (decomp.). (Found : Cl, 29 11. $C_{21}H_{25}O_2N_3Cl_4$ requires Cl, 28.8%).

3-*Methoxy*-2 : 4-*dichloro*-5-(γ-*piperidinopropyl*)-*aminoacridine dihydrochloride* was obtained by first refluxing a mixture of the acid chloride (0.9 g.), dry benzene (30 c.c.) and γ-piperidinopropylamine (0.4 g.) for half an hour and then adding $POCl_3$ (5 g.) and refluxing for 7 hours at 110°. After removing benzene and excess of $POCl_3$, the residue was extracted with alcohol. A red solid after long standing was obtained after precipitating it by ether. It was crystallised from a very small quantity of alcohol, m. p. 226°. (Found : N, 8.37 ; Cl, 29 01. $C_{12}H_{27}ON_3Cl_4$ requires N, 8.57 ; Cl, 28.92%).

CHEMISTRY DEPARTMENT
LALAN GOVT. COLLEGE,
BHUJ (KUTCH).

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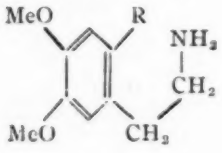
SYNTHESIS OF POSSIBLE AMOEBACIDES. PART I

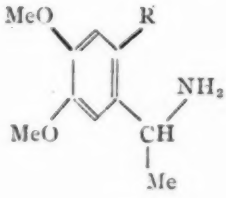
By H. N. Sharma and C. N. Kachru

γ-(2-Alkyl-4 :5-dimethoxyphenyl)-*n*-propylamines with alkyl groups as Me, Et and *n*-Pr have been synthesised through six steps: Veratrole → 4-acylveratrole → 4-alkylveratrole → β-(2-alkyl-4 :5-dimethoxybenzoyl)-propionic acid → γ-(2-alkyl-4 : 5-dimethoxyphenyl)-*n*-butyric acid → γ-(2-alkyl-4 :5 dimethoxyphenyl)-*n*-butyramide → γ-(2-alkyl-4 :5-dimethoxyphenyl)-*n*-propylamine.

Kachru and Pathak (this *Journal*, 1957, **34**, 611, 768) prepared a number of compounds of the types (I) and (II). These could be considered as the hypothetical degradation products of emetine by rupture at various points. In both these types, the compounds (I : R = *n*-hexyl ; II : R = *n*-hexyl) were appreciably active *in vitro* (comparable to that of emetine ; Kaushiva, *J. Sci. Ind. Res.*, 1957, **16C**, 224). If in the type (I), the basic amino group is removed still further away from the nucleus, it is likely to lead to compounds of the type (III). It was considered worthwhile to synthesise these compounds with different alkyl substitutions and to examine their amoebacidal activity. In this communication synthesis of such compounds (where R is Me, Et and *n*-Pr) is described.



(I)



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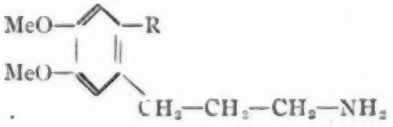
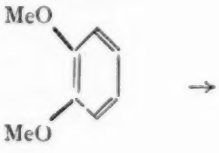
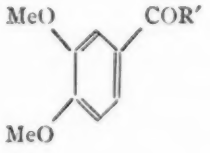


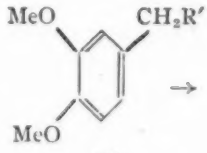
(III)

Synthesis of compounds of the type (III) has been achieved according to the following scheme :



(A)





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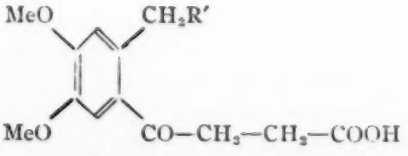
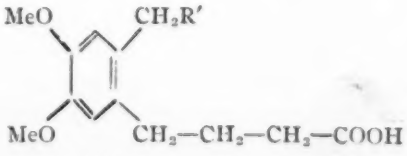
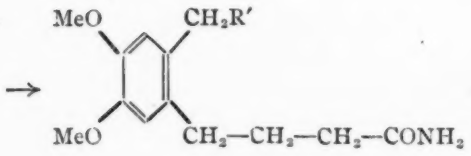


(C)



(D)



(E)

Homoveratrole (B : R′ = H) was prepared by the Clemmensen reduction of vanillin ("Org. Syn.", Vol. 33, p. 17) and subsequent methylation of creosol (Luff, Perkin and Robinson, *J. Chem. Soc.*, 1910, **97**, 1134). The other alkylveratroles (B : R′ = Me, Et) were prepared according to the method described by Kachru and Pathak (*loc.cit.*). The alkylveratroles were condensed with succinic anhydride in nitrobenzene at room temperature, using anhydrous aluminium chloride as the catalyst, to yield the compounds of the type (C) (cf. Ghosh and Robinson, *J. Chem. Soc.*, 1944, 508). The reaction failed when carbon disulphide was used as the solvent. It was also noticed that in nitrobenzene solution the increase of reaction period from 1 to 5 days did not appreciably increase the yields. The yields range from 77-87%. Subsequent conversion of the compounds (C) to those of (D) has been effected by the Clemmensen reduction, using toluene as the auxiliary solvent in excellent yields. The amides of the type (E) have been prepared in good yields by passing dry ammonia gas through the molten acid at 210° for 2 hours. Conversion of the above amides (E) to γ-(2-alkyl-4 : 5-dimethoxyphenyl)-*n*-propylamine (III) has been effected in poor yields by the Hofmann reaction using sodium hypochlorite solution.

EXPERIMENTAL*

β-(2-Methyl-4:5-dimethoxybenzoyl)-propionic Acid (C : R′ = H).—In a 250 c.c. r.b. flask, provided with a reflux condenser and a calcium chloride guard tube, were introduced anhydrous aluminium chloride (20 g.), succinic anhydride (8 g.) and nitrobenzene (50 c.c.). The mixture was shaken thoroughly till the whole of anhydrous aluminium chloride had dissolved. To this mixture homoveratrole (10 g.) was added portionwise with thorough stirring during the course of one hour and then left at room temperature for 24 hours. The solution assumed a dark crimson colour. Next day the mass was decomposed by HCl (conc.) and crushed ice. Nitrobenzene was removed by steam distillation and the residue cooled, when the crude acid solidified. It was filtered, washed successively with HCl (dil.) and water. The crude acid was dissolved in warm dilute sodium carbonate solution and extracted with benzene to remove non-acidic impurities. The alkaline layer was boiled with activated charcoal and filtered. The filtrate on acidification with HCl precipitated the acid which was crystallised from aqueous alcohol as white shining crystals, m.p. 97°, yield 13 g. (78.6%). (Found : C, 61.74 ; H, 6.10. $C_{13}H_{16}O_5$ requires C, 61.90 ; H, 6.35%).

γ-(2-*Methyl*-4:5-*dimethoxyphenyl*)-n-*butyric Acid* (D : R′ = H).—To granulated zinc (350 g.) was added mercuric chloride (35 g.), followed by HCl (conc., 15 c.c.) and water (200 c.c.). It was vigorously stirred for 5 minutes and then allowed to settle. The liquid was decanted off and the amalgamated zinc, thus obtained, was used for

* All melting points and boiling points are uncorrected.

reduction. To this zinc were added *β*-(2-methyl-4 : 5-dimethoxybenzoyl)-propionic acid (52 g.), 1:1 HCl (200 c.c.) and toluene (200 c.c.). The mixture was refluxed for 30 hours, HCl (conc., 25 c.c.) being added after every 6 hours. The toluene layer was separated and the aqueous layer extracted twice with toluene. The combined toluene layer was treated with dilute NaOH solution and the toluene removed by steam distillation. The alkaline layer was refluxed with dimethyl sulphate (15 c.c.), a small amount of more alkali having been added to keep the solution alkaline. A trace of sodium hydrosulphite and animal charcoal were added to the solution which was then heated, cooled and filtered, and the filtrate extracted with benzene to remove non-acidic matter. The desired acid separated as a viscous oil by acidification of the alkaline layer. The oil solidified on keeping which was crystallised from dilute methanol in white needles, m.p. 79°, yield 40 g. (81 6%). (Found : C, 65 19 ; H, 7.32. $C_{13}H_{18}O_4$ requires C , 65.54 ; H, 7.56%).

γ-(2-*Methyl* 4 : 5-*dimethoxyphenyl*)-n-*butyramide* (E : R′=H).—Dry ammonia gas was passed through the above molten acid (D : R′=H ; 25 g) at 200° for 2 hours. The mass while still hot was poured into water with stirring. The separated solid was filtered and washed with water. It was crystallised in short needles from hot water, m.p. 105°, yield 20 g. (80%). (Found : N, 5.90. $C_{13}H_{19}O_3N$ requires N, 5.38%).

γ-(2-*Methyl*-4 : 5-*dimethoxyphenyl*) n-*propylamine* (III : R=Me).—The preceding amide (finely powdered, 15 g.) was added to a solution of sodium hypochlorite (300 c.c., 0.5 *N*) and stirred continually until the whole of the amide had dissolved (3 hours). The clear yellow solution was then warmed on a water-bath for 2 hours, when a brown oil separated out. Solid KOH (40 g.) was added to the solution and heating continued for another hour. It was then cooled and the amine extracted with benzene. The benzene layer was dried over solid KOH, benzene was removed and the residual oil was distilled, b.p. 165°/10 mm, yield 7 g. (53.5 %). The *picrate* was crystallised from dilute alcohol in bright yellow prisms, m.p. 160°. The *hydrochloride* was crystallised from a mixture of ethyl acetate and absolute alcohol, m.p. 201°. (Found : C, 57.92 ; H, 8.32 ; N, 5.64 ; OMe, 25.10. $C_{12}H_{20}O_2NCl$ requires C 58.65 ; H, 8.16 ; N, 5.70 ; OMe, 25.25%).

β-(2-*Ethyl*-4:5-*dimethoxybenzoyl*)-*propionic Acid* (C: R′=Me).—Anhydrous aluminium chloride (19 g.) and succinic anhydride (7 g.) were dissolved in nitrobenzene (100 c.c.). The mixture was kept out of contact with atmospheric moisture and ethylveratrole (10 g.) was added portionwise to it. Subsequent operations were the same as described under compound (C: R′=H). It was crystallised from dilute alcohol in white flakes, m.p. 123°, yield 12 g. (77.5%). (Found : C, 62.75 ; H, 6.45. $C_{14}H_{18}O_5$ requires C, 63.15 ; H, 6.76%).

γ-(2-*Ethyl*-4 : 5-*dimethoxyphenyl*)-n-*butyric Acid* (D: R′=Me).—Amalgamated zinc (350 g.), the preceding acid (C: R′=Me ; 34 g.), 50% HCl (200 c.c.) and toluene (200 c.c.) were refluxed for 34 hours. Subsequent operations were the same as described under compound (D : R′=H). It was crystallised from dilute methanol, m.p. 73°, yield 24 g. (75%). (Found : C, 66.94 ; H, 7.63. $C_{14}H_{20}O_4$ requires C, 66.66 ; H, 7.93%).

γ-(2-*Ethyl*-4 : 5-*dimethoxyphenyl*)-n-*butyramide* (E : R′=Me).—Dry ammonia gas was passed through the above molten butyric acid (D : R′=Me ; 25 g.) at 210° for 2

hours. The hot mass was poured into cold water and thoroughly stirred. The solid was filtered off and crystallised from boiling water in shining needles, m.p. 96-97°, yield 23 g. (92%). (Found : N, 5.49. $C_{14}H_{21}O_3N$ requires N, 5 57%).

γ-(2-Ethyl-4 : 5-dimethoxyphenyl)-n-propylamine (III : R = Et).—The above butyramide (15 g.) was treated with sodium hypochlorite solution (300 c.c., 0.5*N*) in the usual manner, as described under compound (III : R = Me). The amine distilled at 175°/16 mm, yield 7 g. (52%). The *picrate*, prepared in the usual way, was crystallised from dilute alcohol in golden yellow prisms, m.p. 179°. The *hydrochloride* was crystallised from a mixture of ethyl acetate and absolute alcohol, m. p. 158-59°. (Found : C, 60.90 ; H, 8.54 ; N, 5.40 ; OMe, 24.01. $C_{13}H_{22}O_2NCl$ requires C, 60.11 ; H, 8.67 ; N, 5.39 ; OMe, 23.89%).

β-(2-n-Propyl-4 : 5-dimethoxybenzoyl)-propionic Acid (C : R′ = Et).—Succinic anhydride (23 g.) and $AlCl_3$ (anhyd., 60 g.) were dissolved in nitrobenzene (200 c.c.). The mixture was placed in a r.b. flask provided with a reflux condenser and a calcium chloride guard tube, and *n*-propylveratrole (31 g.) was added to it in small portions at a time. The mixture was then kept at room temperature for 45 hours The rest of the procedure was the same as described under compound (C : R′ = H). It was crystallised from dilute alcohol, m.p. 90°, yield 42 g. (87.5%). (Found : C, 63.87 ; H, 7 32. $C_{15}H_{20}O_5$ requires C, 63.3 ; H, 7.14%).

γ-(2-n-Propyl-4 : 5-dimethoxyphenyl)-n-butyric Acid (D : R′ = Et).—The preceding propionic acid (45 g.) was reduced with amalgamated zinc (350 g.) and 50% HCl (200 c.c.) in toluene (200 c.c.) as a solvent for 30 hours in the usual way ; the subsequent operations were the same as described under compound (D : R′ = H). It was crystallised from dilute methanol, m.p. 62-63°, yield 36 g. (85.7%). (Found : C, 66.86 ; H, 8.45. $C_{15}H_{22}O_4$ requires C, 67.67 ; H, 8.27%).

γ-(2-n-Propyl-4 : 5-dimethoxyphenyl)-n-butyramide (E : R′ = Et) was prepared as described under compound (E : R′ = H) from γ-(2-*n*-propyl-4 : 5-dimethoxyphenyl)-*n*-butyric acid (25 g.) and was crystallised from boiling water, m.p. 92-93°, yield 20 g. (80%). (Found : N, 5.18. $C_{15}H_{23}O_3N$ requires N, 5.28%).

γ-(2-n-Propyl-4 : 5-dimethoxyphenyl)-n-propylamine (III : R = *n*-Pr).—The above amide (15 g.) was treated with sodium hypochlorite (300 c.c., 0.5*N*) in the usual manner, as described before. The amine distilled at 165-67°/1 mm, yield 6 g. (46%). The *picrate* was crystallised from boiling water, m.p. 156-57°. The *hydrochloride* was crystallised from a mixture of ethyl acetate and absolute alcohol, m.p. 144°. (Found : C, 61.12 ; H, 8.63 ; N, 5.03 ; OMe, 22.95. $C_{14}H_{24}O_2NCl$ requires C, 61.43 ; H, 8.77 ; N, 5.12 ; OMe, 22.66%).

The authors express their sincere thanks to Dr. Mata Prasad, Vice-Chancellor, Vikram University, for providing research facilities and to Dr. B. Pathak of the Department of Applied Chemistry, Calcutta University, for his keen interest during the course of the investigation.

SCHOOL OF STUDIES (CHEMISTRY),
VIKRAM UNIVERSITY,
UJJAIN (M.P.)

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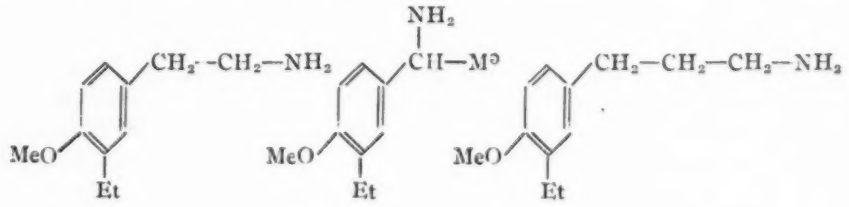
SYNTHESIS OF POSSIBLE AMOEBACIDES. PART II

By S. N. Sawhney and C. N. Kachru

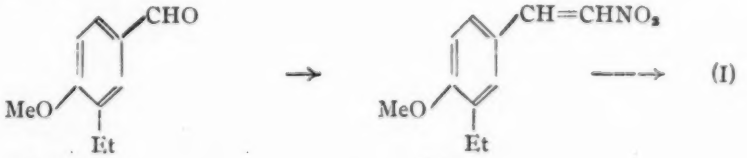
Synthesis of β-(3-ethyl-4-methoxyphenyl)-ethylamine, α-(3-ethyl-4-methoxyphenyl)-ethylamine and γ-(3-ethyl-4-methoxyphenyl)-*n*-propylamine has been made as possible amoebacides.

Kachru and Pathak (this *Journal*, 1957, **34**, 611, 768) prepared β- and α-(2-alkyl-4 : 5-dimethoxyphenyl)-ethylamines of which those containing *n*-hexyl substitution were appreciably active *in vitro* comparable to that of emetine ; Kaushiva, *J. Sci. Ind. Res.*, 1957, **16C**, 224). The object of the present investigation is to find out whether the *o*-dimethoxy group is essential for amoebacidal activity. It is therefore considered worthwhile to prepare similar types of compounds with different phenolic moiety and to examine their amoebacidal activity. In this communication the synthesis of β-(3-ethyl-4-methoxyphenyl)-ethylamine (I), α-(3-ethyl-4-methoxyphenyl)-ethylamine (II) and γ-(3-ethyl-4-methoxyphenyl)-*n*-propylamine (III) is described.



(I) (II) (III)

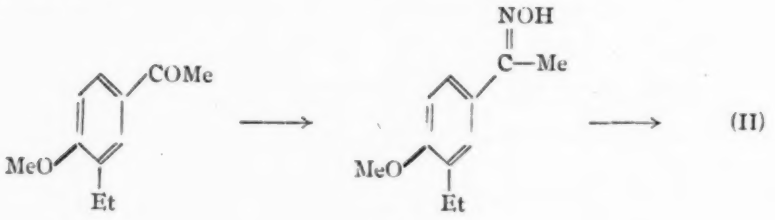
Synthesis of β-(3-ethyl-4-methoxyphenyl)- ethylamine (I) has been achieved according to the following scheme :



(A) (B)

On subjecting *o*-ethylanisole to Gattermann's aldehyde synthesis, as modified by Adams and Levine (*J. Amer. Chem. Soc.*, 1923, **45**, 2373), 3-ethyl-4-methoxybenzaldehyde (A) has been obtained in 15% yield. This aldehyde (A) was condensed with nitromethane to yield 3-ethyl-4-methoxy-β-nitrostyrene (B) in 44% yield. Subsequent reduction to the amine (I) was achieved by the use of lithium aluminium hydride, in 60% yield.

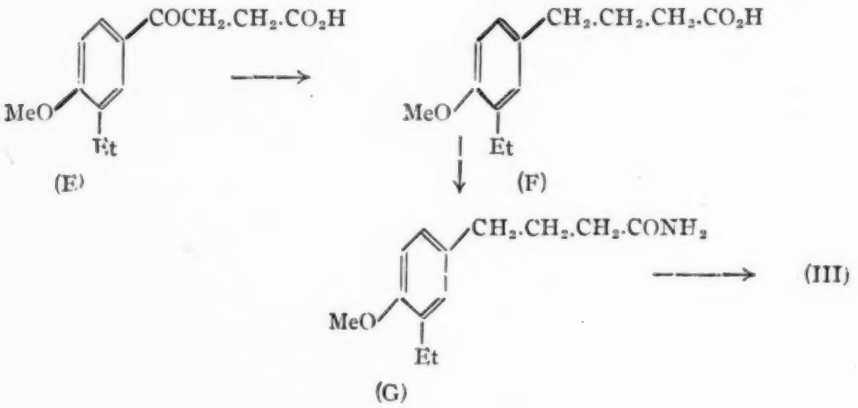
α-(3 Ethyl-4-methoxphenyl)-ethylamine (II) has been prepared according to the scheme shown below:



(C) (D)

o-Ethylanisole on condensing with acetyl chloride in presence of anhydrous aluminium chloride in carbon disulphide yielded 3-ethyl-4-methoxyacetophenone (C) in 45% yield. The demethylation was negligible. This ketone was converted into the corresponding oxime (D) in 80% yield in the usual manner. The oxime on reduction with metallic sodium and super dry alcohol generated the amine (II) in 35% yield.

The synthesis of γ-(3-ethyl-4-methoxyphenyl)-*n*-propylamine (III) is schemed as shown below:



o-Ethylanisole was condensed with succinic anhydride in nitrobenzene solution in the presence of anhydrous aluminium chloride to yield the corresponding keto-acid (E) in 80% yield. The Clemmensen reduction of (E) to γ-(3-ethyl-4-methoxyphenyl)--*n*-butyric acid (F) was accomplished by using toluene as the immiscible solvent. The yield was 65%. The corresponding amide (G) was obtained in 80% yield by passing a current of dry ammonia gas through the molten acid (F) at 200° for 2 hours. The amide (G) on treatment with sodium hypochlorite solution according to the Hofmann reaction gave 40% yield of the desired amine (III).

*EXPERIMENTAL

3-Ethyl-4-methoxybenzldehyde (A).—To a mixture of *o*-ethylanisole (50 g.), zinc cyanide (50 g.) and benzene (400 c.c.), taken in a three-necked flask fitted with a mercury-sealed stirrer and a reflux condenser, cooled in an ice-bath, was passed dry HCl gas for 1 hour. Powdered anhydrous aluminium chloride (70 g.) was then added and the passage of HCl gas was continued. After 3 hours the temperature was raised to 50° which was maintained for 2 hours. Stirring and the passage of HCl gas were continued all the time. The mass was then left overnight. Next day the mass was decomposed by ice and the mixture was refluxed on a water-bath for 2 hours. Benzene layer was separated out and the aqueous layer was extracted twice with benzene. The combined benzene solution was washed with water, dried over calcium chloride and the residue after removal of benzene was distilled under vacuum. The first fraction distilling at 71-72°/1 mm (22 g.) was unchanged *o*-ethylanisole. The aldehyde distilled at 130°/1 mm, yield 10 g. (15%). Its 2:4-*dinitrophenylhydrazone* was crystallised from dilute alcohol, m.p. 216°. The *semicarbazone* was crystallised from alcohol, m.p. 185°. (Found: N, 19.12. $C_{11}H_{13}O_2N_3$ requires N, 19.0%).

3-Ethyl-4-methoxy-β-nitrostyrene (B).—A mixture of 3-ethyl-4-methoxybenzaldehyde (5.46 g.), nitromethane (2.03 g.) and MeOH (6.66 c.c.) was cooled to 5°. To this solution was then slowly added, with vigorous stirring, methanolic solution of NaOH (5 g. in 25 c.c.), previously cooled to 5°. The addition was completed in 10 minutes and the temperature was not allowed to rise above 15°. After an hour ice-cold water was added to dissolve the precipitated solid, and this solution was poured with stirring into a beaker containing 1:1 HCl. It was left for a few hours and the nitrostyrene was then filtered. It was crystallised from dilute alcohol in brownish yellow flakes, m.p. 44°, yield 3 g. (44%). (Found: N, 6.5. $C_{11}H_{13}O_3N$ requires N, 6.7%).

β-(3-Ethyl-4-methoxyphenyl)-ethylamine (I).—A solution of the preceding compound (1.5 g.) in 50 c.c. of anhydrous ether was added dropwise to a well-stirred solution of $LiAlH_4$ (1 5 g.) in 150 c.c. of anhydrous ether, nearly 2 hours being required for complete addition. The mixture was then slowly warmed to gentle refluxing. After cooling, the excess of $LiAlH_4$ was decomposed by dropwise addition of water. The alumina formed was filtered off. The ethereal layer after separation from the aqueous layer was dried over solid KOH. Dry HCl gas was passed through the ethereal solution when the *amine hydrochloride* separated as a white solid. It was crystallised from ethyl acetate, m.p. 125°, yield 1 g. (60%). (Found: C, 61.1; H, 8.4; N, 6.4. $C_{11}H_{18}ONCl$ requires C, 61.2; H, 8.3; N, 6.4%) The *picrate*, prepared in the usual way from the hydrochloride, was crystallised from dilute alcohol, m.p. 191°.

3-Ethyl-4-methoxyacetophenone (C).—Powdered anhydrous aluminium chloride (25 g.) was gradually added to the well-cooled solution of acetyl chloride (15 g.) in CS_2 (100 c.c.) and after keeping it for half an hour, *o*-ethylanisole (25 g.) was slowly added with constant stirring and cooling in ice-water. After keeping

* Melting and boiling points are uncorrected.

overnight, the mixture was warmed on the steam-bath for half an hour. CS_2 was removed by distillation and the residue decomposed by crushed ice. The product was extracted with benzene. The benzene solution was first washed with water, then with sodium hydroxide solution (10%) and finally again with water. The benzene extract was dried over calcium chloride. After removal of benzene, the ketone distilled at 120°/1 mm, yield 14 g. (45 %). (Found: C, 74.3 ; H, 7.9. $C_{11}H_{14}O_2$ requires C, 74.1 ; H, 7.8%). Its 2:4-*dinitrophenylhydrazone* was crystallised from alcohol, m.p. 186°.

3-*Ethyl*-4-*methoxyacetophenone Oxime* (D).—The above ketone (C, 12 g.), hydroxylamine hydrochloride (17 g.) and sodium acetate (36 g.), dissolved in a minimum amount of alcohol, were refluxed for half an hour. On cooling, the oxime separated as a white crystalline solid. It was crystallised from dilute alcohol in white shining flakes, m.p. 93°, yield 10 g. (80 %). (Found : N, 7.2. $C_{11}H_{15}O_2N$ requires N, 7.2%).

α-(3-*Ethyl*-4-*methoxyphenyl*)-*ethylamine* (II).—The above oxime (10 g.) was dissolved in super dry alcohol (100 c.c.). To the hot solution metallic sodium (18 g.) was added rapidly to maintain a vigorous reaction. After whole of the sodium had dissolved, the reaction mixture was cooled, made acidic with HCl (conc.) and alcohol was removed by distillation under reduced pressure. The residual mass was dissolved in water, basified with NaOH solution and the amine was extracted with benzene. The benzene extract was dried over solid KOH, benzene removed and the residual liquid distilled, b.p. 110-15°/1 mm, yield 3 g. (35%). The *picrate* was crystallised from dilute alcohol, m.p. 182°. The *hydrochloride* was crystallised from ethyl acetate, m.p. 190°. (Found: C, 61 0 ; H, 8.5; N, 6.2. $C_{11}H_{18}ONCl$ requires C, 61.2 ; H, 8.3 ; N, 6.4%).

β-(3-*Ethyl*-4-*methoxybenzoyl*)-*propionic Acid* (E).—In a 500 c.c. r.b. flask, provided with a reflux condenser and a calcium chloride guard tube, were introduced anhydrous aluminium chloride (55 g.), succinic anhydride (20 g.) and nitrobenzene (100 c.c.). The mixture was shaken thoroughly till the whole of ahydrous aluminium chloride had dissolved. To this mixture *o*-ethylanisole (25 g.) was added portionwise with thorough stirring during the course of one hour and then left at room temperature for 24 hours. The mixture assumed a crimson colour. The complex was then decomposed by HCl (conc.) and crushed ice. Nitrobenzene was steam-distilled and the residue cooled when the crude acid solidified. It was filtered, washed with HCl (dil.) and then with water. The acid was then dissolved in warm sodium carbonate solution and extracted with benzene to remove non-acidic matter. The alkaline layer was clarified by charcoaling and the acid precipitated out on acidification by HCl. It was crystallised from dilute alcohol, m.p. 149°, yield 35 g. (80%). (Found: C, 65.8; H, 6.8. $C_{13}H_{16}O_4$ requires C, 66.1 ; H, 6.7%).

γ-(3-*Ethyl*-4-*methoxyphenyl*)-n-*butyric Acid* (F).—A mixture of granulated zinc (100 g.), mercuric chloride (10 g.), HCl (conc., 5 c.c.) and 100 c.c. of water was shaken for 10 minutes. The aqueous solution was decanted and the amalgamated zinc, thus obtained, was thoroughly washed with water. To this zinc were added

water (40 c.c.), HCl (conc., 80 c.c.), toluene (50 c.c.) and β-(3-ethyl-4-methoxybenzoyl)-propionic acid (30 g.). The mixture was refluxed for 32 hours, HCl (conc., 25 c.c.) was added after every six hours, cooled and the toluene layer separated. The aqueous layer was twice extracted with toluene. The combined toluene layer was treated with dilute NaOH solution and the toluene was steam-distilled off. The alkaline layer was treated with 10 c.c. of dimethyl sulphate and then heated with activated charcoal, filtered and cooled. The filtrate on acidification gave an oil which solidified on standing to a waxy solid. It was dissolved in benzene, the benzene solution dried over anhydrous magnesium sulphate, benzene removed and the residue distilled, b.p. 184°/1 mm, yield 19 g. (65%). (Found: C, 69.9; H, 8.3. $C_{13}H_{18}O_3$ requires C, 70.2; H, 8.1%).

γ-(3-*Ethyl*-4-*methoxyphenyl*)-n-*butyramide* (G).—Dry ammonia gas was passed through the preceding molten butyric acid (15 g.) at 200° for 2 hours. The mass while still hot was poured into water with stirring. The separated solid was filtered and washed with water and crystallised in white prisms from dilute alcohol, m.p. 101°, yield 12 g. (80%). (Found: N, 6.5. $C_{13}H_{19}O_2N$ requires N, 6.3%).

γ-(3-*Ethyl*-4-*methoxyphenyl*)-n-*propylamine* (III).—Sodium hypochlorite solution (200 c.c., 0.5 *N*) was treated with the above amide (G, 9 g.) with continual stirring till the whole of the amide had dissolved (4 hours). The yellow solution was then heated on a water-bath for half an hour. Solid KOH (30 g.) was added to it and heating continued for 2 hours. The amine separated as an oil which was extracted with ether. To this ethereal extract ether, saturated with hydrochloric acid gas, was added. The *amine hydrochloride* separated out. It was crystallised from ethyl acetate, m.p. 295°, yield 4 g. (40%). (Found: C, 62.4; H, 8.8; N, 6.4. $C_{12}H_{20}ONCl$ requires C, 62.7; H, 8.7; N, 6.1%). The *amine picrate* was crystallised from hot water, m.p. 125°.

The authors express their sincere thanks to Dr. Mata Prasad, Vice-Chancellor, Vikram University, for providing research facilities and to Dr. B. Pathak of the Department of Applied Chemistry, Calcutta University, for his keen interest during the course of this investigation.

School of Studies (Chemistry),
Vikram University, Ujjain,
Ujjain (M.P.)

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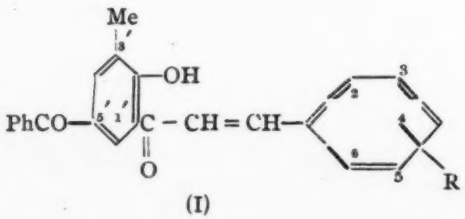
SYNTHESIS OF 2′-HYDROXYCHALKONE DERIVATIVES

By Kumuda C. Amin and G. C. Amin

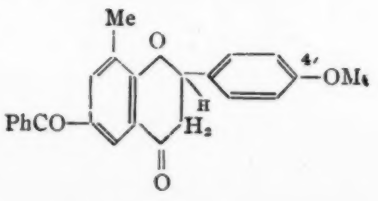
5′-Benzoyl-3′-methyl-2′-hydroxychalkones have been synthesised by condensing 5-benzoyl-3-methyl-2-hydroxyacetophenone with aromatic aldehydes in presence of 40% KOH. Incidentally, 5′-benzoyl-3′-methyl-2′-hydroxy-4-methoxychalkone has been converted into 6-benzoyl-8-methyl-4-methoxy-flavanoid derivatives.

Several substituted derivatives of *o*-cinnamoylphenol or 2′-hydroxychalkone containing the diverse substituents have been extensively investigated. Of these derivatives, those containing one or more hydroxy and/or methoxy groups in one or both phenyl nuclei are receiving particular attention as many naturally occurring chalkones and related flavanoid derivatives are polyhydroxy or polymethoxy compounds.

As a part of the comprehensive work progressing in this laboratory concerning the investigation of 2′-hydroxychalkones and related heterocyclic compounds (Amin *et al.*, *Science & Culture*, 1955, **21**, 268 ; 1957, **23**, 199 ; *Chem. Ber.*, 1957, **90**, 1287 ; *J. Gujarat Univ.*, 1958, **2**, 70 ; *Tetrahedron*, 1958, **2**, 241), we have now synthesised 5′-benzoyl-3′-methyl-2′-hydroxychalkone derivatives. The 5-benzoyl-3-methyl-2-hydroxyacetophenone (Amin and Amin, under publication) was condensed with the appropriate aldehyde in nearly equimolecular proportion. Thus, the presence of benzoyl and methyl groups in 5- and 3- position respectively of the 2-hydroxyacetophenone does not inhibit the formation of the chalkone derivatives, a conclusion, which is in conformation with the similar observations in case of the other substituted 2′-hydroxychalkones. Incidentally, 5′-benzoyl-3′-methyl-2′-hydroxy-4-methoxychalkone was converted into the corresponding 6-benzoyl-8-methyl-4′-methoxyflavanone (Seshadri *et al.*, *Proc. Ind. Acad. Sci.*, 1945, **20A**, 247; 1954, **39A**, 296), flavone (Venkataraman *et al.*, *J. Chem. Soc.*, 1935, 866 ; 1936, 569) and flavonol (Algar and Flynn, *Proc. Roy. Irish Acad.*, 1934, **B42**, 1 ; *Chem. Abs.*, 1935, **29**, 161) smoothly.



(I)



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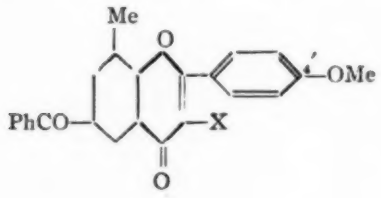

(III)

[X = H and OH]

EXPERIMENTAL

5′-Benzoyl-3′-methyl-2′-hydroxy-4-methoxychalkone (I : R= 4-OMe).—To a solution of 5-benzoyl-3-methyl-2-hydroxyacetophenone (1 g.) and 4-methoxybenzaldehyde (0.6 g.) in ethyl alcohol (20 c.c.) 40% KOH solution (20 c.c.) was added with shaking. The mixture was then heated for 5 minutes when the colour changed from yellow to brownish red. The yellowish solid gradually began to separate after 3 to 4 hours. The reaction mixture was then left overnight at room temperature (25-30°). It was diluted with ice-water and acidified with 1 : 1 HCl. The yellow solid obtained was washed with $NaHCO_3$ solution and water, and was crystallised from acetic acid in yellow needles, m.p. 156°, yield 0.8 g. (Found : C, 77.30 ; H, 5.26. $C_{24}H_{20}O_4$ requires C, 77.43 ; H, 5.37%).

It dissolves very sparingly in NaOH solution with a yellow colour and develops a reddish brown colour with alcoholic ferric chloride and Wilson's boric acid reagent (*J. Amer. Chem. Soc.*, 1939, **61**, 2303). With H_2SO_4 (conc.) it produces a deep red colour with a bluish tinge. It is soluble in common organic solvents.

The other chalkones were prepared similarly and crystallised from acetic as yellow to orange solids. These are shown in Table I.

TABLE I

5′-Benzoyl-3′-methyl-2′-hydroxychalkones (I).

No.	Substituents (R).	M.P.	Formula.	% Carbon.		% Hydrogen.	
				Found.	Calc.	Found.	Calc.
1	Unsubstituted	134°	$C_{23}H_{18}O_3$	82.50	82.57	5.16	5.26
2	2-Hydroxy	202°	$C_{23}H_{18}O_4$	76.97	77.09	5.00	5.03
3	4-Hydroxy	199°	$C_{23}H_{18}O_4$	76.92	77.09	5.00	5.03
4	2-Methoxy	160°	$C_{24}H_{20}O_4$	77.34	77.43	5.27	5.37
5	3 : 4-Methylenedioxy	191°	$C_{24}H_{18}O_5$	74.58	74.76	4.52	4.66
6	3 : 4-Dimethoxy	165°	$C_{25}H_{22}O_5$	74.55	74.63	5.38	5.47
7	3-Methoxy-4-hydroxy	106°	$C_{24}H_{20}O_5$	74.05	74.21	5.03	5.15

The reaction mixtures in case of chalkones No. 2, 3 and 7 were kept at room temperature for about 150 hours.

6-Benzoyl-8-methyl-4′-methoxyflavanone (II).—The alcoholic solution of the above chalkone (I, 0.5 g.) was treated with 10% H_2SO_4 till a faint turbidity had appeared, which was removed by adding an excess of ethyl alcohol. The solution were refluxed on a water-bath for 25 to 30 hours and then concentrated. The yellow solid was crystallised from alcohol in yellowish needles, m.p. 136°. It is insoluble in NaOH. (Found : C, 77.36 ; H, 5.3. $C_{24}H_{20}O_4$ requires C, 77.43 ; H, 5.37%).

6-Benzoyl-8-methyl-4′-methoxyflavone (III : X = H).—The chalkone (I, 0.5 g.) and selenium dioxide (0.5 g.) in dry *iso*amyl alcohol (20 c.c.) was refluxed at 150-60° for 18 to 20 hours. The filtrate obtained after removing precipitated selenium was steam-distilled to remove *iso*amyl alcohol. A dark brown solid separated which was crystallised from acetic acid in yellowish needles, m.p. 225°, yield 0.3 g. It is insoluble in alkali and is negative to alcoholic ferric chloride test. (Found : C, 77.59 ; H, 5.05. $C_{24}H_{18}O_4$ requires C, 77.62 ; H, 5.10%).

6-Benzoyl-8-methyl-4′-methoxyflavonol (III : X = OH).—To an alcoholic solution of the chalkone (I, 0.5 g.) 5% NaOH solution (20 c.c.) was added. The deep red solution was cooled in ice and 17% H_2O_2 (5 c.c.) was added to it. The reaction mixture was kept in ice for 2 hours, during which solid particles separated. It was then left overnight at room temperature whereupon the colour of the mixture turned orange. It was diluted with ice and water and acidified with HCl. The yellow solid was washed with water and crystallised from acetic acid in yellow granules, m.p. 252°, yield 0.2 g. It is soluble in excess of alkali, and develops a greenish blue fluorescence with H_2SO_4 (conc.). (Found : C, 75.98 ; H, 4.58. $C_{24}H_{18}O_5$ requires C, 76.15 ; H, 4.66%).

M. R. Science Institute,
Gujrat College,
Ahmedabad-6.

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COMPOUNDS OF ANTIMONY TRICHLORIDE WITH AMINES AND HETEROCYCLIC BASES

By Sarju Prasad, G. B. Punna Rao, Suresh Kumar, V. Rama Reddy and Kamta Prasad Kacker

The organic derivatives of antimony trichloride have been prepared by the action of some mono-, di-, secondary and tertiary amines and heterocyclic bases on $SbCl_3$ in benzene; their properties have been studied and structures discussed.

Schiff (*Ann. chim. phys.*, 1864, **131**, 161; *Compt. rend.*, 1863, **56**, 1905; *Ber.*, 1901, **34**, 805) obtained quinolino-antimony trichloride, $SbCl_3.C_9H_7N$, and trianilino-antimony trichloride by treating antimony trichloride with respective bases in benzene. May (*J. Chem. Soc.*, 1911, **99**, 1383) added aniline to antimony trichloride in benzene till the precipitate first formed redissolved; the solution on evaporation gave a crystalline compound, $SbCl_3.3C_6H_5NH_2$, which, when washed with petroleum ether, gave a compound, $SbCl_3.C_6H_5NH_2$. He concluded that the first compound was formed by taking two molecules of aniline of crystallisation. By a similar method he prepared *o*-toluidine, *p*-toluidine and *p*-chloroaniline derivatives of antimony trichloride also. Duff and Bills (*ibid.*, 1929, 411) obtained *tris*-hexamethylenetetramine-antimony trichloride, $SbCl_3.3C_6H_{12}N_4$, by mixing alcoholic solutions of both the substances. Grey (*ibid.*, 1926, 3174) prepared a large number of addition compounds of antimony trichloride with diazotised diamines in HCl. Belladan and Astengo (*Atti R. Accad. Lincei*, 1923, *v*, **32**, 491) obtained $SbCl_3.HCl.(BzNH_2)_2$ by the action of benzamide on $SbCl_3$. Bruni and Manuenl (*Z. Elektrochem.*, 1905, **11**, 554) observed that when a solution of antimony trichloride in formamide was diluted, a compound having the composition ranging between $SbCl.(NH.COH)_2$ and $Sb^{\prime\prime\prime}(NH.COH)_3$, was obtained.

Experimental

Antimony trichloride and the amines and heterocyclic bases used were of Merck's or B.D.H.'s 'Pure' quality, and benzene was dehydrated and redistilled.

Antimony trichloride and the organic components were dissolved in benzene separately and the compounds were prepared by two different methods. In the first case, an excess of the $SbCl_3$ solution was added to the solution of the organic component till the precipitation was complete; it was filtered, washed free of $SbCl_3$ with benzene. In the second case, an excess of the organic component was added to the $SbCl_3$ solution till the precipitate first formed either dissolved or changed in colour. If the precipitate dissolved, the solution was concentrated on a sand-bath till it reappeared. The precipitate was purified by washing with benzene. The products obtained were dried at the room temperature except in a few cases where they were dried in vacuum.

Antimony was estimated as Sb_2S_3 and chlorine as AgCl. The organic matter was found by difference in all cases except three where nitrogen was estimated by Kjeldahl's method and the percentage of the organic matter calculated.

TABLE Ia

Antimony trichloride wi'h primary amines.

$SbCl_3$: NH_2 group = 1 : 1.

Amines.	Compounds formed.	Colour.	M.P.	% Antimony.		% Chlorine.		% Org matter (by diff.).	
				Found.	Calc.	Found.	Calc.	Found.	Calc.
α-Naphthylamine	$SbCl_3.C_{10}H_7NH_2$	Grey	160°	31.27	32.79	29.33	28.64	30.40	38.57
β-Naphthylamine	$SbCl_3.C_{10}H_7NH_2$	Buff	175°	33.66	32 79	28.25	28 64	38.09	38.57
m-Toluidine	$SbCl_3.C_6H_4.CH_3NH_2$	Light brown	125°	37.53	36.33	31.18	31.74	31.29	31.93
o-Anisidine	$SbCl_3.C_6H_4\ O.CH_3NH_2$	Light pink	153°	35.70	34 66	29 90	30.28	34.40	35.06
p-Anisidine	$SbCl_3.C_6H_4O.CH_3NH_2$	Blackish white	135-40°	35 51	34 66	29.84	30 28	34.65	35.06
o-Phenetidine	$SbCl_3\ C_2H_5.O\ C_6H_4NH_2$	Rosy	112°	35.24	33.33	30.24	29.11	34.52	37.56
p-Phenetidine	$SbCl_3.C_2H_5\ O.C_6H_4NH_2$	Grey	178°	31.73	33 33	30.54	29 11	37.73	37.56
Benzylamine	$SbCl_3.C_6H_5CH_2NH_2$	Light yellow	212°	36 15	36.32	32.45	31.72	31.40	31.96
Phenylhydrazine	$SbCl_3.C_6H_5NH\ NH_2$	Light pink	140°	37.31	36.21	31.01	31.63	31.68	32.16
n-Butylamine	$SbCl_3.CH_3.CH_2\ CH_2$-CH_2NH_2	White	144°	42.40	40.42	34.76	35 31	22.84	24.27

TABLE Ib

Antimony trichloride with primary amines.

$SbCl_3$: NH_2 group = 1 : 3.

Amines.	Compounds formed.	Colour.	M.P.	% Antimony.		% Chlorine.		% Org. matter (by diff.).	
				Found.	Calc.	Found.	Calc.	Found.	Ca'c.
α-Naphthylamine	$SbCl_3\ (C_{10}H_7NH_2)_3$	Pink	175°	18 67	18.51	16.51	16.16	64 82	65.33
β Naphthylamine	$SbCl_3.(C_{10}H_7NH_2)_3$	Bluish white	158°	17.85	18.51	15.63	16.16	66 52	65.33
m-Toluidine	$SbCl_3.(C_6H_4CH_3NH_2)_3$	Rosy	118°	23.45	22.16	20.02	19.36	56.53	58 48
o-Anisidine	$SbCl_3.(C_6H_4OCH_3NH_2)_3$	Pink	146°	19.83	20.38	17.17	17.80	63.00	61.82
p-Anisidine	$SbCl_3.(C_6H_4OCH_3NH_2)_3$	Greenish white	155°	21.28	20.38	18.38	17 80	60.34	61 82
o-Phenetidine	$SbCl_3.(C_2H_5O.C_6H_4NH_2)_3$	White	130°	18.54	19.03	17.07	16.63	64.39	64.34
p-Phenetidine	$SbCl_3.(C_2H_5O.C_6H_4NH_2)_3$	Pink	185°	18.85	19.03	17.08	16.63	64.07	64.34
Benzylamine	$SbCl_3.(C_6H_5CH_2NH_2)_3$	Yellow	210°	22.04	22.15	19.34	19.35	58.62	58.50
Phenylhydrazine	$SbCl_3.(C_6H_5NHNH_2)_3$	Pale yellow	188°	22.85	22.04	19 81	19.25	57.34	58.71
m-Xylidine	$SbCl_3.[C_6H_3(CH_3)_2NH_2]_3$	Yellow-brown	152°	20.00	20.57	17.90	17.97	62.10	61.46
*iso*Propylamine	$SbCl_3.[(CH_3)_2CH.NH_2]_3$	Yellow-orange	150°	30.68	30.02	26.37	26.22	42 95	43.76

TABLE IIA

Antimony trichloride with diamines.

$SbCl_3$: NH_2 group = 1 : 1.

Diamines.	Compounds formed.	Colour.	M.P.	% Antimony. Found.	% Antimony. Calc.	% Chlorine. Found.	% Chlorine. Calc.	% Org. matter Found.	% Org. matter Calc.
o-Phenylenediamine	$2SbCl_3.C_6H_4.(NH_2)_2$	Dark pink	76°	43.01	43.14	37.71	37.68	19.28	19.18
p-Phenylenediamine	$2SbCl_3.C_6H_4(NH_2)_2$	Violet pink	147°	44.21	43.14	37.32	37.68	18.47	19.18
Benzidine	$2SbCl_3.(C_6H_4NH_2)_2$	Light pink	150°	38.97	38.02	32.81	33.21	28.22	28 27
o-Tolidine	$2SbCl_3.(NH_7CH_3C_6H_3)_2$	Do	194°	37.27	36.42	31.44	31.81	31.29	31.77
o-Dianisidine	$2SbCl_3.(CH_3O.NH_2C_6H_3)_2$	Grey	210°	35.63	34.75	31.13	30.35	33.24	34.90
Ethylenediamine	$2SbCl_3.NH_2CH_2CH_2NH_2$	White	137°	48.06	47.17	40.60	41.19	11.34	11.64
1 :2-Naphthylenediamine	$2SbCl_3.C_{10}H_6(NH_2)_2$	Reddish brown	139°	40.00	39.62	34.93	34.60	25.07	25.78

TABLE IIB

Antimony trichloride with diamines.

$SbCl_3$: NH_2 group = 1 : 3.

Diamines.	Compounds formed.	Colour.	M.P.	% Antimony. Found.	% Antimony. Calc.	% Chlorine. Found.	% Chlorine. Calc.	% Org. matter. Found.	% Org. matter. Calc.
o-Phenylenediamine	$2SbCl_3\ [C_6H_4(NH_2)_2]_3$	Light rosy	110°	31.17	31.19	27.48	27.24	41.35	41.57
p-Phenylenediamine	$2SbCl_3.[C_6H_4(NH_2)_2]_3$	Dark violet	206°	30.37	31.19	27.08	27.24	42 55	41.57
Benzidine	$2SbCl_3.[(NH_2C_6H_4)_2]_3$	Pale white	220°	24.53	24.15	20.01	21.09	55.46	54.76
o-Tolidine	$2SbCl_3.[(NH_2CH_3C_6H_3)_2]_3$	White	210°	22.79	22.27	18.87	19.46	58.34	58,27
o-Dianisidine	$2SbCl_3.[(CH_3O.NH_2-C_6H_3)_2]_3$	Dirty white	195°	20.47	20.47	17.35	17.88	62.18	61.65

TABLE IIIA

Antimony trichloride with secondary and tertiary amines.

$SbCl_3$: NH_2 group = 1 : 1.

Amines.	Compounds formed.	Colour.	M.P.	% Antimony. Found.	% Antimony. Calc.	% Chlorine. Found	% Chlorine. Calc.	% Org. matter. Found.	% Org. matter. Calc.
Diphenylamine	$SbCl_3.(C_6H_5)_2NH$	Brown	165°	31.97	30.66	26 51	26 78	41.52	42.56
o-Methyltoluidine	$SbCl_3.C_6H_4CH_3NHCH_3$	Brown	142°	35.86	34.86	29.90	30 46	34.24	34 68
Butylaniline	$SbCl_3.C_6H_5NH.C_4H_9$	White-green	162°	32.15	32.25	27.86	28.16	39 99	39.59
Dimethylaniline	$SbCl_3.C_6H_5N(CH_3)_2$	Dirty green	85°	34.17	34.85	31.01	30 45	34.82	34.70
Diethylaniline	$SbCl_3.C_6H_5N(C_2H_5)_2$	White	120-25°	32.31	32.27	28.01	28.18	39.68	39.55
Dimethyl-*o*-toluidine	$SbCl_3.C_6H_4CH_3N(CH_3)_2$	Green	90°	33.39	33.52	29.00	29.27	36.61	37.21
Diethyl-*o*-toluidine	$SbCl_3.C_6H_4CH_3N(C_2H_5)_2$	Light rosy	130°	31.45	31.11	27.49	27.17	41.06	41.72
Diethyl-*p*-toluidine	$SbCl_3.C_6H_4CH_3N(C_2H_5)_2$	Flesh colour	121°	31.09	31.11	27.21	27.17	41.70	41.72
Benzylidene-alaniline	$SbCl_3.C_6H_5CH\ NC_6H_5$	Brownish yellow	133°	30.82	29.75	25.52	25.99	43.66	44.26
p-Aminodiethyl-aniline	$2SbCl_3.C_6H_4NH_2N(C_2H_5)_2$	...	115°	39.10	39.24	33.98	34.18	26.92	26.48

TABLE IIIB

Antimony trichloride with secondary and tertiary amines.

$SbCl_3$: NH_2 group = 1 : 3.

Amines.	Compounds formed.	Colour.	M.P.	% Antimony. Found.	Calc.	% Chlorine. Found.	Calc.	% Org. matter. Found.	Calc.
Methylaniline	$SbCl_3.(C_6H_5NH.CH_3)_3$	White	...	22.57	22.15	19.07	19.35	58.36	58.50
Butylaniline	$SbCl_3.(C_6H_5NH.C_4H_9)_3$	White	158°	18.12	18.02	15.57	15.73	66.31	66.25
Diethylamine	$SbCl_3.(C_2H_5NH.C_2H_5)_3$	Brownish white	...	27.38	27.20	23 92	23.76	48.70	49.04
Dimethylaniline	$SbCl_3.(C_6H_5N(CH_3)_2)_3$	Dark green, viscous	...	20.82	20.58	17.76	17 97	61.42	61.45
Diethylaniline	$SbCl_3.[C_6H_5N.C_2H_5)_2]_3$	Yellow, viscous	...	18.41	18.02	15.24	15.73	66.35	66.25
Diethyl-*p*-toluidine	$SbCl_3.[C_6H_4CH_3N(C_2H_5)_2]_3$	Yellow, viscous	...	17.22	16.97	14.90	14.81	67.88	68.22

TABLE IV

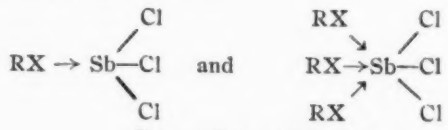
Antimony trichloride with aminobenzoic acids and heterocyclic bases.

$SbCl_3$: NH_2 group = 1 : 1.

Aminobenzoic acids and heterocyclic bases.	Compounds formed.	Colour.	M.P.	% Antimony. Found.	Calc.	% Chlorine. Found.	Calc.	% Org. matter. Found	Calc.
o-Aminobenzoic acid	$SbCl_3.NH_2C_6H_4\ COOH$	White	96°	33.36	33.34	29 00	29.12	37.64	37 54
m-Aminobenzoic acid	,, ,,	White	144°	33.56	33.34	28.96	29.12	37.48	37.54
Pyridine	$SbCl_3.C_5H_5N$	White	151°	40.80	39.65	34.08	34.63	25.12	25.72
α-Picoline	$SbCl_3.C_5H_4.CH_3N$	White	131°	39.09	36.76	32 73	32.11	28.18	31.12
Quinoline	$SbCl_3.C_6H_4C_3H_3N$	Brown	154°	35.11	34.08	29.32	29.77	35.57	36.15
Piperidine	$SbCl_3.C_5H_{10}NH$	White	141°	40.09	38.88	33.34	33.96	26.57	27 14

DISCUSSION

Though antimony has five electrons in the outermost orbit, yet only three are utilised for valency purposes in the formation of trivalent antimony compounds, the other two remaining inert. According to Sidgwick ("Electronic Theory of Valency", 1927) the covalency of six is curiously rare in the case of antimony, and it generally forms the stable four-covalent octet only by co-ordination. In the case of amines, however, two types of compounds have been obtained in which the ratios of $SbCl_3$ to the amino group are as 1 : 1 and 1 : 3, and can be represented as



[X = NH_2, NH or N]

The formation of two types of compounds of $SbCl_3$ has also been observed by Vanstone (*J. Chem. Soc.*, 1925, 550) in the case of benzanilide and by Kelley and McCuskar (*J. Amer. Chem. Soc.*, 1943, **65**, 1307) who obtained two stable dioxanates having the compositions, $2SbCl_3.3C_4H_8O_2$ and $SbCl_3.2C_4H_8O_2$.

All the compounds are stable in the dry atmosphere at the room temperature, but begin to hydrolyse slowly on exposure to moisture (diamino compounds being an exception) or when treated with water, dilute NaOH or dilute Na_2CO_3 solution. On boiling, however, these hydrolyse quickly and SbOCl and Sb_2O_3 are precipitated. All the compounds are insoluble in common organic solvents, but dissolve in mineral acids. On heating with sodalime, the corresponding amines separate out and condense on the cooler parts of the tube. Most of the compounds decompose at the melting point.

The 1 : 1 compounds are more stable than 1 : 3 compounds. In each of the series the stability of the compounds is in the following order : primary > secondary > tertiary.

Besides, the diamino compounds are the most stable. It has also been observed that the *ortho* compounds provide more stable products than the *para* compounds and that heavier the molecule of the amine, greater is the stability of the compound formed. Thus, $SbCl_3.C_6H_5N(C_2H_5)_2$ is more stable than $SbCl_3.N(CH_3)_2$ and diethyl-*p*-toluidine derivative, $SbCl_3$-*p*-$C_6H_4CH_3.N(C_2H_5)_2$ has been prepared, but the dimethyl-*p*-toluidine derivative, could not be isolated under identical conditions.

The 1 : 3 compounds are less stable than 1 : 1 compounds, but on repeatedly washing with benzene, these give the same composition and, hence, it cannot be said definitely that 1 : 3 compounds are formed by the addition of two molecules of amines to 1:1 compounds, as observed by May (*loc. cit.*). It is very likely that these are formed due to variation in acceptor property of antimony.

In the case of heterocyclic bases, 1 : 3 compounds are not formed and 1 : 1 compounds are similar to those obtained with primary amines. *Ortho*- and *meta*- aminobenzoic acids give only 1 : 1 compounds, which shows that only the NH_2 group is responsible for the formation of the compounds and the carboxylic group does not react at the ordinary temperature.

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CHEMICAL LABORATORIES,
BANARAS HINDU UNIVERSITY,
VARANASI-5.

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SHORT NOTES

SYNTHESIS OF 2-AMINO-2-CARBOXYETHANE SULPHONAMIDE

By B. V. Bhide

Cystine was converted by Hess (*J. Amer. Chem. Soc.*, 1934, **56**, 1421) into its hydantoin. A suspension of the hydantoin in water was chlorinated to afford 5-(chlorosulphonyl) methylhydantoin (m. p. 146-47). This was converted into its amide; the 5-(aminosulphonyl) hydantoin (m. p. 246-48°) was then hydrolysed by $Ba(OH)_2$. The hydrolysate gave on evaporation *in vacuo* the ammonium salt of 2-amino-2-carboxyethane sulphonamide, m.p. 247°. The salt lost ammonia on warming for several hours at 110° and repeated evaporation from its aqueous solution. Attempts to prepare the corresponding pyrimidine and thiazole derivatives failed. The substance did not show any antibacterial property against *Staph. aureus* or *M. tuberculosis*.

5-(*Chlorosulphonyl*)-*methylhydantoin*.—Cystine hydantoin (20 g.) was suspended in 200 c.c. of water and chlorine passed in, with cooling, till the liquid smelt of chlorine. Ethyl acetate was added when most of the solid went into solution. The aqueous layer was extracted several times with ethyl acetate. The combined ethyl acetate extract was dried over magnesium sulphate, and ethyl acetate was removed under reduced pressure. The residue was recrystallised from ethyl acetate, m.p. 146-47°. (Found: N, 13.10; Cl, 16.9. $C_4H_5O_4N_2ClS$ requires N, 13.2; Cl, 16.7%).

5-(*Aminosulphonyl*)-*methylhydantoin*.—A suspension of 5-(chlorosulphonyl)-methylhydantoin (10 g.) in dry ether was saturated with dry ammonia for 1 hour. The solid was filtered and washed with ethyl acetate, yield 4 g. It was recrystallised from water, m.p. 246-48°. (Found: N, 21.9. $C_4H_7O_4N_3S$ requires N, 21.8%).

2-*Amino-2-carboxy - ethane Sulphonamide*.—5-(Aminosulphonyl)-methylhydantoin (2 g.) was heated with $Ba(OH)_2$ (2.2 g.) in 20 c.c. of water, in a sealed tube at 150° for 2 hours. To the contents of the tube ammonium carbonate (1 g.) was added and the barium carbonate filtered off. The filtrate was concentrated repeatedly with addition of water and evaporated to dryness. The solid was very soluble in water m.p. 245-46° (decomp.). (Found: N, 18 6; S, 21.1. $C_3H_8O_3N_2S$ requires N, 18.5; S, 21.05%).

Maharaja Pratapsingh Chemical Laboratory,
Sir Parashurambhau College
Poona-2.

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A NEW METHOD OF PREPARATION OF URANIUM^{IV} OXYFORMATE

By Balaram Sahoo and D. Patnaik

Rosenheim (Seaborg and Katz, "The Actinide Elements", 1954, 1st ed., p. 159) prepared uranium^{IV} oxyformate by refluxing uranium tetrachloride with formic acid till hydrogen chloride was completely eliminated. He obtained the compound having the formula $UO(HCOO)_2,3H_2O$. The present authors (*Curr. Sci.*, 1958, **27**, 243) reported the preparation of uranium^{IV} oxyformate having the formula $UO(HCOO)_2$, $1.5H_2O$ by the photolysis of a saturated solution of uranyl formate, formic acid and alcohol by sunlight. In absence of alcohol, while the reduction of U^{VI} to U^{IV} is complete on exposure to sunlight for 12-15 hours, precipitation of uranium^{IV} oxyformate does not occur. If this product of photolysis, which contains the UO^{2+} and $HCOO^-$ with excess of formic acid and water, is distilled at a low pressure, uranium^{IV} oxyformate having the formula $UO(HCOO)_2$, $1.5H_2O$ is obtained. The photolytic product, reported by us earlier, though produces the same compound, yet it is not quantitative, as much of the reduced uranium remains in solution. But the method described here, in which the distillation of the photolytic product is carried out, uranium^{IV} oxyformate is obtained quantitatively. The formic acid, which is distilled off, can be used again for a fresh preparation.

Uranyl nitrate and formic acid were of E. Merck, G.R. and E.P. quality respectively. Preparation of uranyl formate and its saturated solution and its exposre to sunlight for complete reduction of uranium^{VI} to uranium^{IV} were made as described eariler (*loc. cit.*).

Procedure.—The reduced solution was distilled at a low pressure at 65°-70°, when formic acid and water distilled off and a pasty mass remained behind. The pasty mass, when dried over fused calcium chloride and solid sodium hydroxide in a vacuum desiccator overnight, furnished a pale green powder.

The determinations of molecular weight and of the uranium and formate contents were carried out as described previously (*loc. cit.*).

The analytical data recorded in Tables I and II show that the compound obtained is $UO(HCOO)_2$, $1.5H_2O$. The compound, when heated in vacuum at 150-60°, gave the anhydrous uranium^{IV} oxyformate.

TABLE I

Compound taken.	U_3O_8 found.	M.W. Calc.	Compound taken.	U^{4+} by Hatt's method Found.	Calc.
0.1652 g	0.1252	370.0	0 3326 g.	0.2100	0.2134
0.2480	0.1884	369.6	0.2122	0.1349	0.1361
0.2670	0.2006	373.6	0.1838	0.1158	0.1174
0.2007	0.1510	373.0	0.2862	0.1807	0.1836

TABLE II

Compound taken.	U by Jones reductor. Found.	Calc.	Compound taken.	Formate by $KMnO_4$. Found.	Calc.
0.2610 g.	0.1675 g.	0.1674	0.2299 g.	0.0559	0.0558
0.2037	0.1311	0.1307	0.2336	0.0564	0.0567
0 1895	0.1222	0.1216	0.2350	0 0568	0.0570
0.1874	0.1209	0.1202	0.1845	0.0441	0.0447

The compound has assumed importance as we have reported the preparation of uranium tetrafluoride by the action of hydrofluoric acid on it at ordinary temperature (*Curr. Sci.*, 1959, **28**, 16)..

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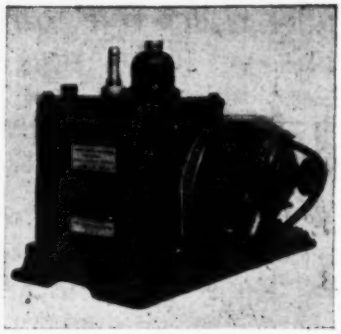

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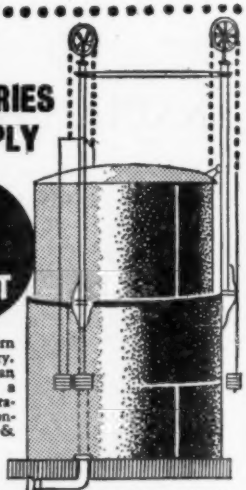

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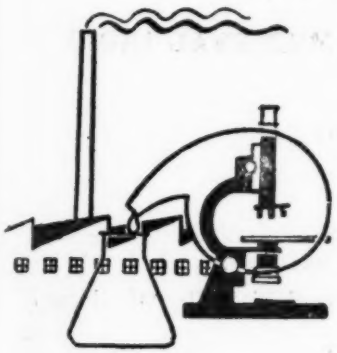

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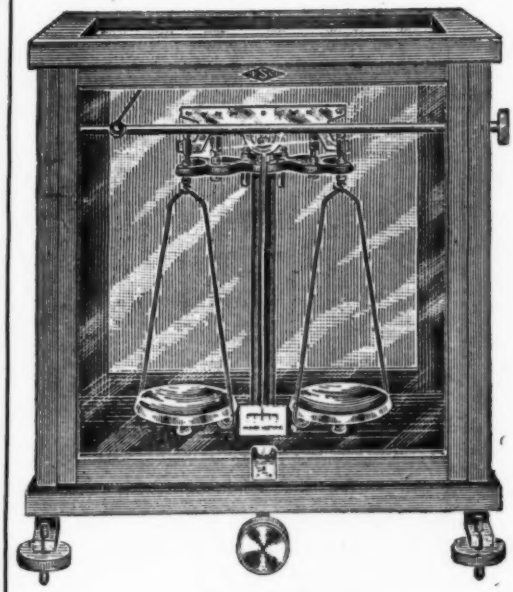

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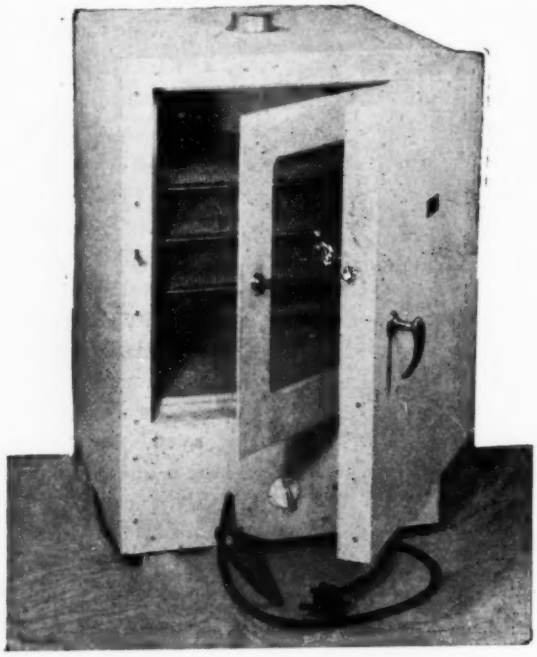

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